FINAL REPORT

WORK ASSIGNMENT NO. 109
EPA CONTRACT NO. 68-01-7331

RECORDS COMPILATION
PRESQUE ISLE STATE PARK
ERIE, PENNSYLVANIA

SUBMITTED TO:

CDM FEDERAL PROGRAMS CORPORATION
SUITE 200
13135 LEE JACKSON MEMORIAL HIGHWAY
FAIRFAX, VIRGINIA 22033

SUBMITTED BY:

VERSAR INC.
6850 VERSAR CENTER
SPRINGFIELD, VIRGINIA 22151

AUGUST 3, 1987

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## EXECUTIVE SUMMARY

In the early 1970s, a foul-smelling, sulfur-laden, black liquid began discharging near Beach No. 7 at Presque Isle State Park located in Erie, Pennsylvania. The area remained somewhat of a mystery until 1979 when the Pennsylvania Department of Environmental Resources (PADER) unearthed the leaking, abandoned natural gas well that was the source of the noxious seep. The formation which produced the seeping liquid was the upper Silurian Bass Island dolomite at a depth of 1,521-1,586 feet. The discharge released hydrogen sulfide into the atmosphere and other hazardous substances to the soil.

Early investigations conducted by the Erie County Department of Health in the early 1970s, by PADER from 1979 to 1983, and by U.S. EPA and PADER from 1983 to the present, have sought to better define the cause of the discharge and potential for similar discharges to create environmental and public health hazards in the Erie area. The central issue in these investigations has been whether the discharge was natural phenomena or if it was related to the deep well injection of approximately 1.1 billion gallons of spent pulping liquor into the Bass Island Formation during 1964-1971. These two alternative explanations for the seeping gas well were investigated by some of the most sophisticated chemical testing and mathematical simulations of the deep well injection system currently available.

The state of Pennsylvania plugged the seeping gas well in the fall of 1982. PADER's environmental consultant, Roy F. Weston, Inc., investigated Beach No. 7 and determined that no health hazards were present as a result of the seepage which had already taken place. Clean sand was brought in to cover the area surrounding the plugged well. The Beach No. 7 well site was placed on the National Priority List in September 1983 because the U.S. EPA and U.S. Geologic Survey were concerned that the same noxious fluid might also be seeping from other abandoned gas wells of similar age and construction in the Erie area. The U.S. EPA's Field Investigation

Team sampled domestic water wells in the Erie area near similar abandoned oil and natural gas wells and determined that none of these water wells showed any effects that would indicate that the nearby oil and gas wells were leaking.

Other oil and gas wells in the Erie area were sampled to determine whether the Bass Island Formation fluid from these wells were chemically similar to the fluid which had seeped from the Beach No. 7 well. Wells were sampled very near to the underground injection wells and from a well located far beyond the area where the spent pulping liquor could be expected to have moved within the Bass Island Formation. Chemical testing was unable to positively link the discharge with the injected spent pulping liquor. Driller's logs of oil and natural gas wells from large portions of Erie County indicate 204 occurrences of "black water," a Bass Island Formation fluid which naturally resembles the noxious fluid encountered at the Beach No. 7 well. Additionally, the adjacent counties in New York also have similar formation fluids in the Bass Island Formation.

Mathematical simulations of the deep well injection system's effect on the formation pressures of the Bass Island dolomite were also unable to positively link the deep well injection system with the seeping Beach No. 7 natural gas well. These simulations indicate that it would be quite difficult for the chemical constituents of the injected spent pulping liquor to have both migrated approximately 4 miles from the injection wells to the Beach No. 7 well and have maintained enough pressure to cause the seepage for 10 years following the sealing of the injection wells. The simulations do suggest that the injection liquor could not be expected to have moved far enough to explain the occurrences of "black water" in the 204 wells in Erie County or other wells in New York.

The chemical testing provided enough information to establish that the fluid which was formerly seeping form the Beach No. 7 well was no more hazardous than the formation fluids which oil and gas drillers normally encounter in routine drilling in Erie County. Oil and gas drilling is regulated by PADER's Bureau of Oil and Gas Management, and procedures for responding to problems associated with hazardous formation fluids are already in place.

The only known problems associated with hazardous fluids seeping from abandoned oil and natural gas wells in the Erie area was the Beach No. 7 well. The health hazard from this well was eliminated when PADER plugged the well in 1982. Further attempts to better define the source of the seepage at that well would involve drilling very expensive monitoring wells which might not resolve the issue, and could present an unnecessary environmental risk. This report recommends that the site be delisted from the National Priorities List because no clear threat currently exists to public health or the environment. The Superfund regulations specifically provide for immediately relisting the site if any problems related to the site are encountered in the future.

## 1.0 INTRODUCTION

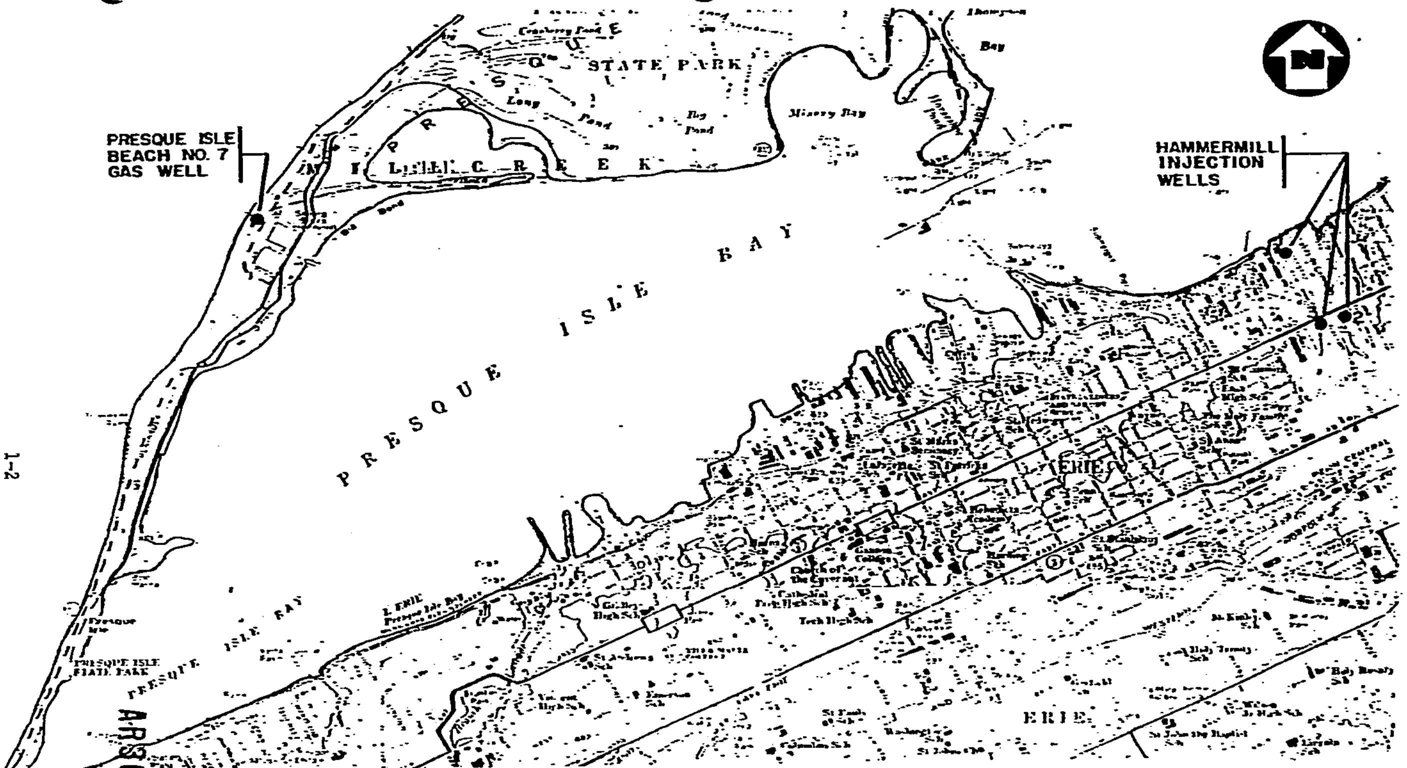
### 1.1 Background

*The Presque Isle site is on the National Priorities List (NPL) and* is located in Presque Isle State Park near Erie, Pennsylvania (Figure 1-1). In the early 1970s, the Erie County Health Department noted a seep near Beach No. 7 that was discharging a noxious, hydrogen sulfide-bearing, black liquid. The discharge released hydrogen sulfide to the air and other hazardous substances to the soil and shallow ground water.

Investigations by the Pennsylvania Department of Environmental Resources (PADER) from 1979 to 1982 revealed that the source of the discharge was from an abandoned natural gas well and that the black fluids were emanating from the Upper Silurian Bass Island Formation at a depth of 1,523 feet (Figure 1-2). The gas well was buried at the time the discharge was first noticed and was originally described as a "seep." Following the discovery of the well, references to the "seep" generally refer to the discharge from the annulus of the gas well. The deeper Silurian Lockport Formation (at a depth of 1,960 feet), contains a naturally occurring, hydrogen sulfide- bearing brine ("black water" in driller's terminology). A central issue of the investigations to date has been whether the fluid discharging from the Bass Island Formation is a natural brine or is related to deep-well- injected wastes.

Hammermill Paper Company operated three underground injection wells from 1964 to 1971 and injected 1.09 billion gallons of neutral sulfite pulping liquor into the Bass Island Formation. The nearest Hammermill well is located 4.2 miles from the well at Beach No. 7 (Figure 1-1). PADER felt that there was a reasonable cause and effect relationship between Hammermill's injection well program and the discharge at Presque Isle.

PADER formally contacted U.S. Environmental Protection Agency (EPA) Region III during 1982 to assist with the sampling program conducted




REFERENCE
7.5' USGS TOPOGRAPHIC MAPS, ERIE SOUTH, ERIE-NORTH AND SWANVILLE QUADRANGLES, PENNSYLVANIA, DATED 1957, PHOTOREVISED 1969 AND 1975, SCALE 1" = 2000'.

FIGURE 1-1
MAP SHOWING LOCATION OF PRESQUE ISLE,
CITY OF ERIE, PENNSYLVANIA
(Shoener-EPA, 10/85)

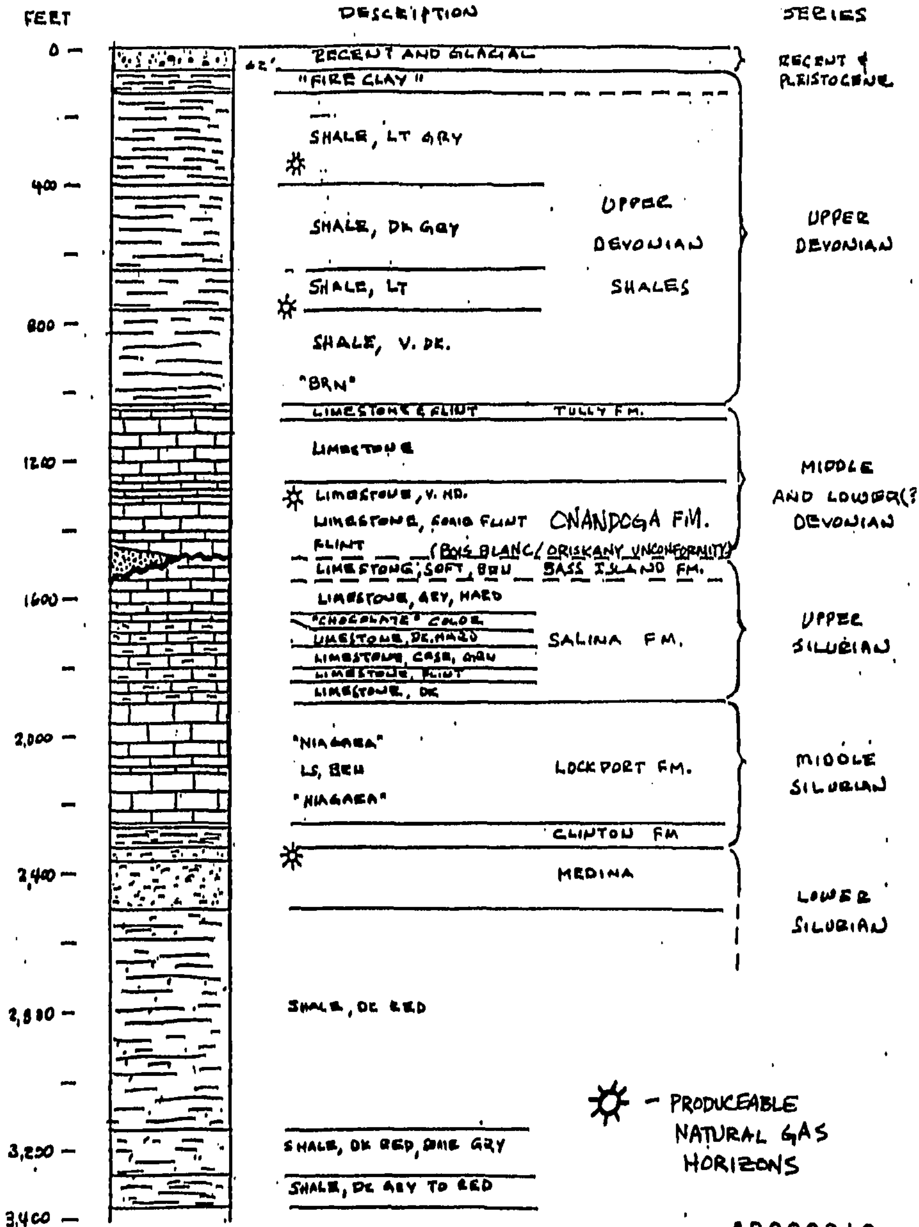



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FIGURE 1-2
GENERALIZED STRATIGRAPHIC SECTION AT ERIE, PENNSYLVANIA
(Click-USGS, 12/28/82)

during the plugging of the Beach No. 7 well. The site was placed on the NPL in September 1983 because of the potential for similar releases from other improperly plugged oil and gas wells in the surrounding area.

EPA conducted a number of additional studies to better define the cause of the discharge and to determine whether there were any potential environmental impacts from similar discharges. Hammermill Paper Company's consultants, the International Technology Corporation (IT - formerly D'Appolonia), also conducted numerous investigations. The results of these studies are included in a remedial investigation/feasibility study (RI/FS) document titled "Summary of Investigations and Recommendations for Further Action" (Shoener-EPA, 10/85). Available chemical evidence provides ambiguous information on the source of the discharge. However, these investigations have found that the discharge at Presque Isle was an unusual event and that the immediate threat to the public from the Beach No. 7 well was eliminated when the well was plugged in the fall of 1982.

The RI/FS (Shoener-EPA, 10/85) recommended that (1) local oil and gas drillers be notified that a hydrogen sulfide-bearing brine is present in the Bass Island Formation and that drillers should be prepared to seal wells in the formation if a hydrogen sulfide release occurs, (2) oil and gas wells drilled through the Bass Island Formation should be monitored for high pressures and the occurrence of "black water" or hydrogen sulfide, and (3) the current information does not warrant the costs and environmental risks associated with engaging in a drilling program to conclusively define the origin of the discharge at the Beach No. 7 well.

## 1.2 Project Approach

Versar received a work assignment (TES III, WA No. 109) to perform a records compilation for the Presque Isle site. Since 1979, a very large number of documents have been produced from PADER and EPA investigations. Versar has reviewed these documents to assess (1) potentially responsible party (PRP) involvement, (2) potential actions that EPA Region III should address in a record of decision (ROD), and (3) whether appropriate criteria for delisting the site from the NPL exist.

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The legal issues involved are complex. The principal issue of whether the fluid discharging from the Beach No. 7 well has a natural origin is rooted in the definitions of pollutants or contaminants and hazardous substances identified under CFR 300.6, which exempts natural gas and natural gas liquids. These definitions affect the applicability of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as defined under CFR 300.3(a)(2). Since the legal problems involved are beyond the scope of this report, the discussion will be confined to the technical issues as a means of developing a detailed factual basis for legal interpretation.

The volume and complexity of the currently available information requires a three-fold treatment. First, a historical summary will highlight the previous investigations and the evolution of thought concerning the site. Next, in a discussion of the relevant technical issues, we will examine the hypotheses raised by PADER, Hammermill and IT consultants, and EPA researchers. Lastly, an evaluation of the present migration pathways and potential threats to the population will be developed based on the historical and technical discussions.

Reference citations for documents that specifically address the Presque Isle site or Hammermill injection program include the author, affiliation, and date. For general references, we will cite only the author and date. The following acronyms for affiliations are used throughout this report:

PADER - Pennsylvania Department of Environmental Resources
EPA - U.S. Environmental Protection Agency
HML - Hammermill Paper Company
USGS - U.S. Geological Survey
PDOH - Pennsylvania Department of Health
EDOH - Erie County Department of Health

The use of affiliations and complete dates within citations is intended to assist readers in understanding the context of the reference.

All personal communications referenced in this report, unless otherwise noted, occurred between the party cited and Mr. Noel Simmons of Versar Inc.

The reference list at the end of this report describes the most relevant documents concerning the Presque Isle site. The purpose of this report is to provide a detailed review of these reference documents to enable further interpretation of them. The documents cited in this report will be specifically flagged in the organized site files to be delivered to EPA separately; Versar strongly recommends that interested parties read these documents.

## 2.0 SITE LOCATION AND DESCRIPTION

Presque Isle State Park and the Beach No. 7 gas well are located in northern Erie County, Pennsylvania (Figure 1-1). Presque Isle is a public recreational area used for picnicking, swimming, and fishing. The park contains an ecological reservation and is a natural habitat for deer, squirrel, water fowl, and many herbivorous species (Ecology & Environment-EPA, 3/23/82). Presque Isle is a low-lying (elevation approximately 580 feet above mean sea level) sand spit composed of coarse-grained glacial sands that is connected to the mainland by a narrow causeway (Figure 1-1). Elevation references within this report are made relative to mean sea level with the exception of depths within wells which are referenced from the surface.

The city of Erie, Pennsylvania, is located on a terraced bluff at an elevation of 600-850 feet above mean sea level. The elevations of the Hammermill injection wells are between 630 and 650 feet (D'Appolonia/IT-HML, 3/83). The three injection wells are located 4.2 miles east of the Beach No. 7 well on Presque Isle. A more complete discussion of the Hammermill injection wells is contained in Section 3.0.

The overburden consists of glacial deposits that produces usable quantities of ground water. However, the bedrock consists of shale, and in drilled wells, especially those near Lake Erie, one commonly encounters salty waters, sulfurous waters, or even gas at shallow depths (Pennsylvania Topographic and Geologic Survey, 1967). In Mill Creek Township, to the west of the City of Erie, the glacial sediments are roughly 50-100 feet thick (USGS, 1952), as shown in Figure 2-1. Near the home of Mr. Timothy Saylor (formerly of the Erie County Health Department and now with Hammermill), fresh water occurs at 25 feet, "black water" occurs at 40 feet, and gas occurs in Devonian shales at 200 feet (Walker-PADER, 1/19/79).

Thousands of oil and gas wells have been drilled in Erie County. Drilling and production began as early as 1821 in the shallow Devonian

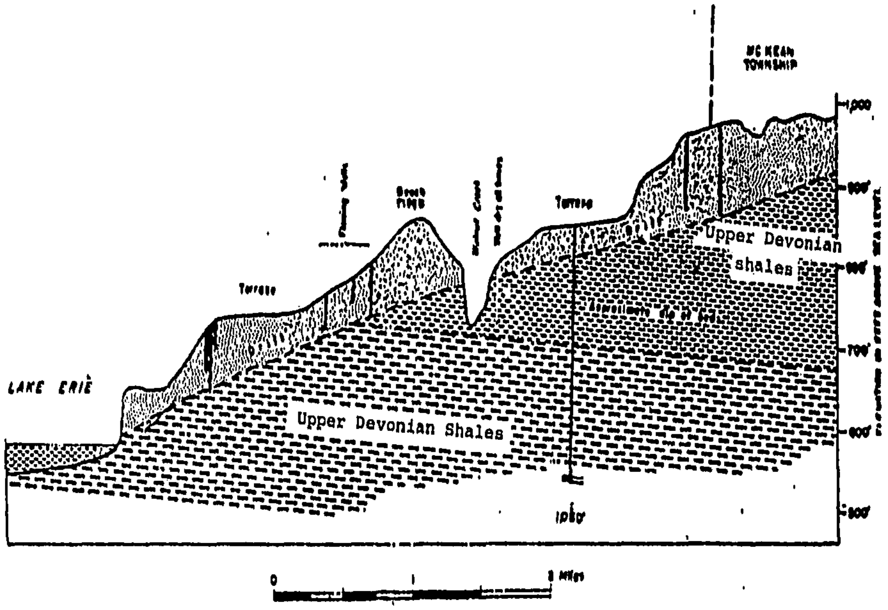


FIGURE 2-1
CROSS SECTION THROUGH WESTERN EDGE OF MILL CREEK TOWNSHIP
SHOWING THICKNESS OF GLACIAL DRIFT
(USGS, 1952)

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shale reservoirs (Pennsylvania Topographic and Geologic Survey, 1977). By 1889, 200 wells had been drilled in the City of Erie (Pennsylvania Topographic and Geologic Survey, 1889). In 1889, the first deep well was drilled to a depth of 4,460 feet. In 1910, the "City of Erie Presque Isle #1" (referred to in this report and previous reports as the Beach No. 7 well) was drilled to a depth of 3,572 feet (Walker, 1/19/79). A more detailed description of this well and Erie County geology is contained in Section 4.0.

Although there are numerous shallow Devonian gas wells in the City of Erie and the surrounding area, these wells do not penetrate the Bass Island Formation. Oil and gas wells must reach the Devonian Onandoga Formation to provide the potential for migration of fluids from the Bass Island Formation. The Onandoga Formation is porous in some locations; above the Onandoga, there is a 1,000-foot section primarily composed of shale (Figure 1-2). Figure 2-2 shows the locations of deep wells surrounding the City of Erie (i.e., those wells that penetrate the Onandoga or deeper formations).

At the surface, the Presque Isle site consists of a single plugged natural gas well. However, under CFR 300.3(a)(2), the boundaries of the site can be interpreted as containing any area of Erie County where there are "releases or substantial threats of releases of hazardous substances into the environment, and releases or substantial threats of releases of pollutants or contaminants which may present an imminent and substantial danger to public health or welfare."

The only confirmed surficial flows of the Bass Island fluid are at the Beach No. 7 well and at the Hammermill 1 injection well when that well failed in 1968 due to corrosion of the casing (Shoener-EPA, 10/85). If discharges similar to those at the Beach No. 7 well were to occur, current information indicates that ground water contamination would only occur in a highly localized area around improperly cased or sealed wells (Shoener-EPA, 10/85).

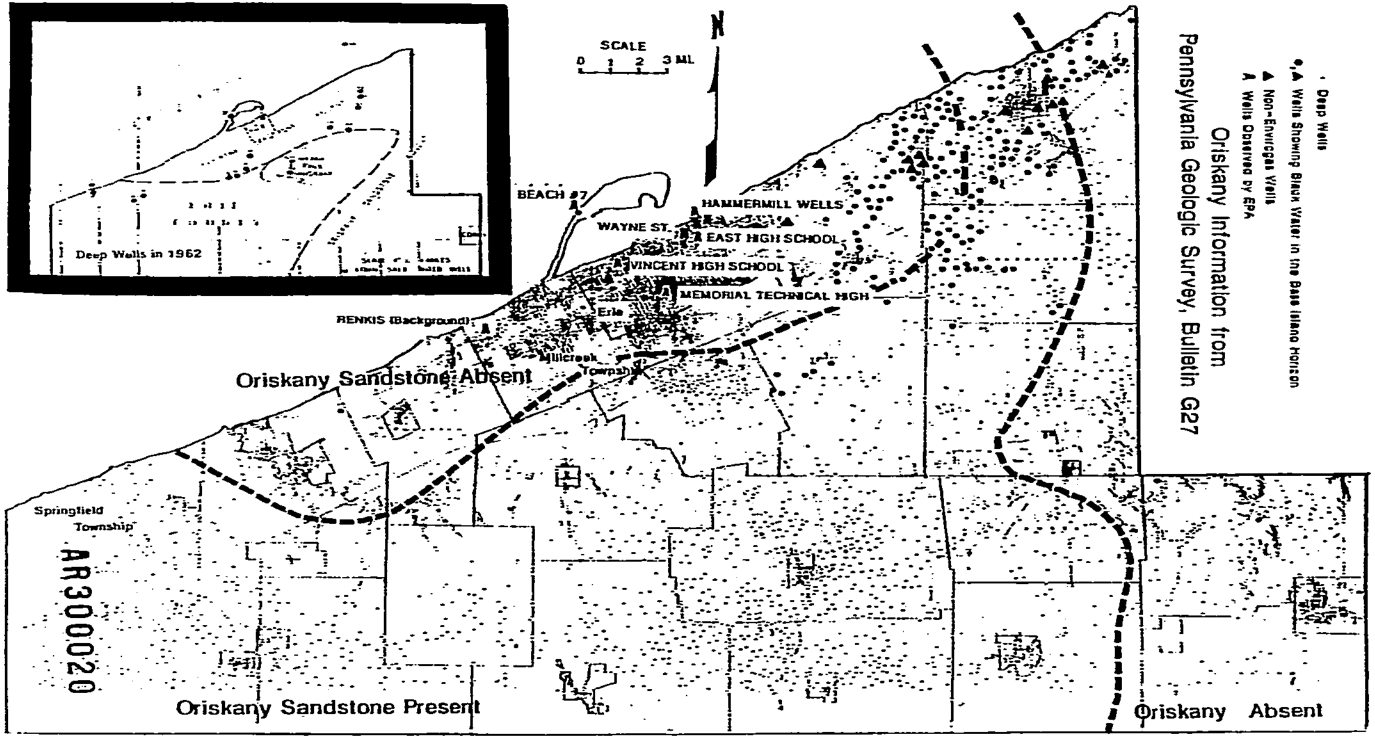





FIGURE 2-2
DEEP WELLS IN ERIE COUNTY, PENNSYLVANIA,
(Adapted from Pennsylvania Geological Survey, 1962.)

## 3.0 SITE HISTORY

### 3.1 Hammermill Pulping Process (Before 1963)

Throughout most of its history, the Hammermill Plant at Erie, Pennsylvania, has produced pulp for its fine printing and writing papers by the sulfite pulping process which involves using Canadian softwoods. In the late 1940s, the company began a research program to develop a pulping process that could make use of hardwoods, which were abundant in the Erie area. This research led to the development of Hammermill's patented Neutracel process, a neutral sulfite process. The pulping liquor from the softwood process was used by a Hammermill subsidiary to make various saleable products, but the liquor from the Neutracel process was unsuitable for this purpose (Brown and Spalding-HML, 12/66).

Initially, Hammermill discharged its spent pulping liquor directly to Lake Erie. However, pulping liquor generates a great deal of foam when agitated. The prominent plume of foam from Hammermill's discharge drew the attention of the media and the Pennsylvania Sanitary Water Board (Truman Andrews-HML, personal communication, 12/8/87). In September 1961, the Sanitary Water Board ordered Hammermill to abate its Lake Erie discharge by September 1963--a deadline that was later extended to the end of 1965 (Brown and Spalding-HML, 12/66).

Hammermill completed its switch from a softwood pulping process (Conifracel process) to the Neutracel process on March 21, 1966 (Brown-HML, 5/19/66). Spent Neutracel pulping liquor was deep-well injected after filter pretreatment. Spent Conifracel pulping liquor could not be injected due to a chemical incompatibility which caused a calcium coating in the filters (diatomaceous earth), resulting in a shutdown (Clista-PDOH, 2/3/66).

Hammermill experienced other problems with the chemical composition of its pulping wastes during the preliminary research and development of its injection program. Originally, Hammermill's pulping liquor contained paper filler materials, such as clay and titanium dioxide from the recycled paper mill water. Before any liquid could be deep-well injected into the subsurface, it must be free of suspended particulate matter and lack chemical incompatibilities that would form solid (pore-plugging) products. In order to achieve proper liquor clarity for filtering and injection, Hammermill was forced to abandon the use of the recycled mill water in favor of city water to collect its pulping liquor (Brown and Spalding-HML, 12/66). Therefore, paper filler materials were never injected, because they would have forced the well system to shut down.

3.2 Hammermill Injection Program (1963-1971)

Hammermill contracted Dow Industrial Service to perform a feasibility study for deep well disposal of the Neutracel pulping liquor (Dow-HML, 11/19/62). This report evaluated potential reservoirs, legal issues, the potential for ground-water contamination, and design considerations. The Dow report (11/19/62) discusses several wells where fluid flow from the Bass Island Formation was considerable, including the Beach No. 7 well on Presque Isle and the "Erie deep test well" in the City of Erie approximately 1.5 miles from the Hammermill plant. The large flow of fluids from the Bass Island and Lockport Formations was the basis for Dow's recommendation that these formations be tested for suitability as disposal reservoirs (Dow-HML, 11/19/62). Dow (HML, 11/19/62) further recommended that the Erie deep test well be kept under surveillance, because it may not have been properly sealed.

Dow drilled an initial test well, the Hammermill 1 well, during January and March 1963 to a depth of 2,302 feet through the Lockport Formation. According to Brown and Spalding (HML, 12/66), "saltwater was encountered from the Bass Island Formation and the water filled the hole at a rapid rate." The same phenomenon was encountered in the Lockport Formation (Brown and Spalding-HML, 12/66). These fluids rose in the hole to within 150 feet of the surface (Walker-PADER,1/19/79). An attempt to acidify the Lockport Formation to increase its porosity and permeabiltity was unsuccessful. However, the Bass Island Formation was acidified, and on the basis of its enhanced porosity and permeability, it was selected as the disposal reservoir (Brown and Spalding-HML, 12/66).

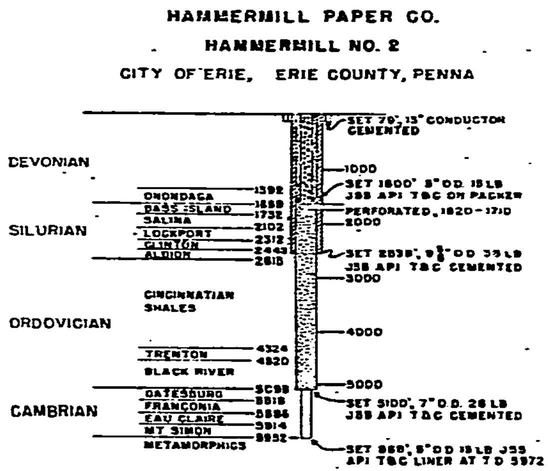
The Hammermill deep well disposal system also involved injecting wastes into the Bois Blanc Formation, which is a cherty, sandy limestone that unconformably overlies the Bass Island Formation (Walker-PADER, 8/15/83). This formation was not recognized in the Erie area in the early 1960s, and the depth interval containing this formation was included in Hammermill's permits to inject wastes from the State of Pennsylvania (D'Appolonia/IT-HML, 10/27/83).

During initial injection testing, abnormally high injection pressures were experienced as a result of bacterial growth within the geological formation. Therefore, a biocide (Busan 881) was added to the injected fluid. The treatment was included as part of the routine injection program (Brown and Spalding-HML, 12/66).

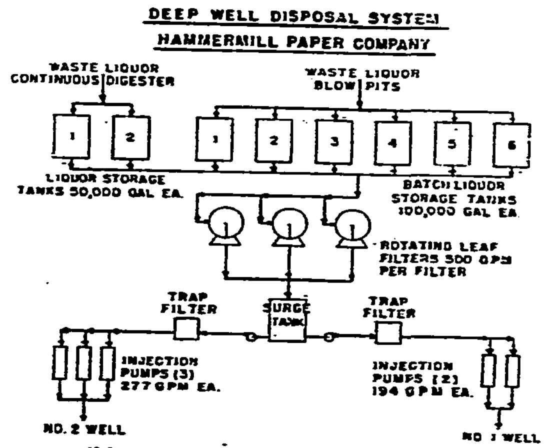
Hammermill drilled its second injection well, Hammermill No. 2, beginning in July 1964. This well was drilled through the sedimentary rock column to the metamorphic rocks at a depth of 5,972 feet to test deeper horizons (Brown and Spalding-HML, 12/66). The Cambrian Gatesburg Formation was tested and found to be unsuitable for injection (D'Appolonia/IT-HML, 3/83). Therefore, the Bass Island horizon was perforated, and the deeper horizons were cemented off (Waldron and Associates-HML, 6/13/72). Hammermill well 3 was drilled and completed in the Bass Island dolomite in 1968. All three injection wells were properly permitted under the prevailing Pennsylvania regulations:

Hammermill 1 - I.W.P. No. 36110 (August 20, 1963)
Hammermill 2 - I.W.P. No. 36515 (July 30, 1965)
Hammermill 3 - I.W.P. No. 3681005 (July 11, 1968)

Pulping liquor was collected from the digesters in a series of 100,000-gallon tanks, filtered into a surge tank, through trap filters to positive displacement piston pumps, each having a rated capacity of 194 gallons per minute (gpm) and a pressure rating of 1,590 pounds per square inch (psi) (see Figure 3-1, Brown and Spalding-HML, 12/66). From the pumps, the spent pulping liquor was injected into the Bass Island




(a) —Cross section of the formations under Erie, Pa., and construction of Well No. 2. (Ft × 0.3 = m; in. × 2.54 = cm.)




(b) —General scheme of surface treatment facilities for Hammermill deep-well disposal system.

FIGURE 3-1
(a) CROSS SECTION OF FORMATIONS UNDER ERIE, PENNSYLVANIA, AND CONSTRUCTION OF WELL 2.
(b) SCHEME OF SURFACE TREATMENT FACILITIES FOR HAMMERMILL DEEP-WELL DISPOSAL SYSTEM.
(Brown and Spalding-HML, 12/66)

Formation through one of three injection wells. Table 3-1 contains pertinent information on the operation of the three wells and a comparison to the Beach No. 7 well at Presque Isle.

On April 14, 1968, the Hammermill 1 injection well experienced a blowout and a drop in injection pressure when the 7-inch casing failed. The injected pulping liquor flowed from the well at a rate of 200 gpm into Lake Erie for 6 days until the well was brought under control (Lyon-PDOH, 4/17/68). Immediate measures were taken to protect nearby property from overspraying: (1) A 55-gallon drum was used to prevent the spray from being picked up by the wind, (2) a barrier of pulpwood was erected, and (3) a ditch was dug to route the pulping liquor/brine to the lake until the well could be sealed (PDOH, 4/18/68).

PDOH (4/18/68) also mentions that a slight leak was detected in the 5-inch and 7-inch casings of Hammermill 2. Ground water in the vicinity of both of these wells probably would not have been jeopardized by these failures (except for surficial runoff), because the 9 5/8-inch outer casing was breached in neither Hammermill 1 or 2. Hammermill stopped injecting into well 2 in September 1968 and replaced this well with Hammermill 3, which went into service in July 1968 (D'Appolonia/IT-HML, 3/83). Hammermill No. 1 was repaired by replacing the failed casing with fiberglass to prevent future corrosion difficulties (HML, 5/17/68). Hammermill chose not to put well 2 back into operation, because the facility was preparing to change the chemical process used in its pulping liquor, to open a wastewater treatment plant, and to plug the injection system (Brown-HML, 11/18/68).

During the early phases of its injection program, Hammermill recognized the need to develop an alternative pulping process that would enable it to recycle the pulping liquor (Brown and Spalding-HML, 12/66). The recylcing effort would allow Hammermill to terminate their injection activity. During 1968, Hammermill formally announced its intentions to the state (Brown-HML, 11/18/68). PADER requested (Westlund-PADER,

TABLE 3-1
DESCRIPTION AND INJECTION HISTORY
OF HAMMERMILL WELLS 1, 2 AND 3
AND OF THE PRESQUE ISLE WELL
(Adapted from D'Appolonia-HML, 3/83)

| DESCRIPTION | UNIT | HAMMERMILL WELLS | | | PRESQUE ISLE WELL |
|---|---|---|---|---|---|
| | | NO. 1 | NO. 2 | NO. 3 | |
| Year Drilled | - | 1963 | 1964 | 1968 | 1910 |
| Surface Elevation | feet above MSL | 629.3 | 650 | 647 | 580 |
| Approximate Depth of Bass Island Fm. (top to bottom) | feet | 1611-1688 | 1658-1732 | 1586-1737 | 1521-1586* |
| Primary Injection Zone(1) | feet | 1620-1670 | 1620-1710 | 1620-1720 | -(2) |
| Period of Injection | - | 5/64-5/71 | 9/65-9/68 | 7/68-5/71 | - |
| Date of Sealing | - | 9/72 | 9/72 | 9/72 | - |
| Pump Capacity | gpm | 388 | 831 | 831 | - |
| Operating Pump/ Surface Pressure | psi | 1,150 | 1,250 | 1,250 | - |
| Total Injected Volume | gallons | $4.5 \times 10^8$ | $3.0 \times 10^8$ | $3.5 \times 10^8$ | - |
| Estimated Average Injection Rate(3) | gpm | 121 | 189 | 237 | - |

(1)Injection feasibility tests were also performed on the Lockport Formation in Well No. 1 and in the Gatesburg Formation in Well No. 2 (Figure 3). Results indicated these formations were not satisfactory for injection zones.

(2)"-" indicates not applicable.

(3)Estimated from total injected volume during period of injection.

* Corrected based on Walker (PADER, 8/15/83)

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1/28/79) and received (Waldron-HML, 6/13/72) from Hammermill a complete set of well records for the injection system. Permits for the plugging were obtained from the state (R. Walker-PADER, 7/20/72), and approval was received from the Chief of the Bureau of Groundwater Quality in Meadville (Westlund-PADER,8/8/72). The wells were plugged in September 1972 (D'Appolonia/IT-HML, 3/83).

The change from Neutracel I to Neutracel II was a switch from a neutral-sulfite-based liquor which could not allow liquor recycling (Brown and Spalding-HML, 12/66) to an alkaline-based liquor which could be recycled (A. Brosig-HML, personal communication, 12/8/86). Because of this switch, an actual sample of the injection liquor was unavailable for chemical analysis when PADER later became interested in the seep problem during 1979.

### 3.3 Early Complaint History - Erie County Investigators (Circa 1970-1972

In the early 1970s, Presque Isle State Park personnel received complaints about a seep of foul-smelling, black water near the western edge of a parking lot at Beach No. 7 (Walker-PADER, 8/15/83). The area was near several outhouses (D'Appolonia-HML, 10/27/83). According to Mr. Timothy Saylor (HML, personal communication, 12/8/86), who was then an inspector for the Erie County Health Department (EDOH), the seep was sampled, and it was determined that the seep was not sewage, because it lacked coliform bacteria. Mr. Saylor has since left the Erie County Health Department and is now employed by Hammermill.

Mr. Saylor stated that he sent the records of these early investigations to John Walker at PADER in Harrisburg during 1979 (HML, personal communication, 12/8/86). However, Mr. Walker stated that he had never received them (HML, personal communication, 12/12/86). During later investigations, the PADER files were duplicated for use by EPA Region III. Versar obtained all of the duplicates and was unable to locate any of these early complaints or analytical results within the

PADER files. Versar contacted the Erie County Health Department. Versar was informed that without the exact date of the sampling, these documents would be difficult to locate within their files and that many files were purged in 1973.

The issue of whether the seep existed prior to the early 1970s has been a matter of dispute between PADER and Hammermill's consultants, D'Appolonia/IT. Walker (PADER, 8/15/83) contends that the seep was not present before the Hammermill injection program began largely because (1) the 1910 well log for the Beach No. 7 well (discovered later) does not mention surficial flows of Bass Island Formation brines, (2) a road was built over the wellhead in 1924, and the drainage pipe attached to the well drained the 4-inch casing, not the 6 1/4 to 8 5/8 inch annulus from which the Bass Island Formation fluid flow was observed during 1979-1982, (3) Beach No. 7 receives heavy use and there are no records of complaints before 1970, and (4) no action was taken to remedy the seep during major improvements to the park area during the late 1950s (if the seep existed).

In rebuttal, Hammermill noted that the seep is located very near to outdoor privies and that park visitors might naturally have confused the hydrogen sulfide odors from the seep with the odors from nearby outhouses. D'Appolonia felt that the proximity of the outhouses "makes any attempt to establish the initiating date of well seepage by examining dates of odor complaints speculative" (HML, 10/27/83). Mr. Saylor stated that before its early 1970 sampling trip, the Erie County Health Department suspected that the seep might have been sewage. However, the black particulate that settled out of solution in field observations, coupled with the lack of coliform bacteria in later analytical results, positively ruled out sewage as the cause (Saylor-HML, personal communication, 12/8/86). The source of the fluid was not defined by the Erie County Health Department, but because the seep was not sewage, the agency felt that although the odors were unpleasant, the fluid did not constitute a clear and present health risk to park visitors (Saylor-HML, personal communication, 12/8/86).

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The confusion between hydrogen sulfide and sewage odors is a plausible explanation for the lack of complaints before 1970. During the early stages of the PADER investigation at Beach No. 7, investigators examined and sampled another seep near the lighthouse on Presque Isle, which was described as "a seep of black, foul smelling water, that had blackened the ground in a way similar to the Beach No. 7 seep, and that USGS geologists Jack Gallaher and David Richards had detected a gas odor there" (Walker-PADER, 5/9/80). Subsequent analytical testing confirmed that it was high in fecal coliform bacteria and BOD, which indicate a sewage origin (Walker-PADER, 5/9/80). The outhouses at Beach No. 7 were removed sometime during the mid-1970s (Saylor-HML, personal communication, 12/8/86).

### 3.4 Early PADER Investigation (December 1978 - February 1979)

PADER was alerted to the seep at Beach No. 7 by a request from the regional superintendent who reported that "over the past year an odor problem has developed and is becoming more intense" (Martz-PADER, 12/7/78). The seep area was 4 feet by 40 feet, and gas that smelled like hydrogen sulfide was bubbling over an area of approximately 1 square foot. The black material was observed to settle to the bottom of collection jars (Martz-PADER, 12/7/78). A request for investigative assistance was referred to Mr. John Walker, a geologist in the Bureau of Forestry, Minerals Section. Oil and gas wells on state park property are under the jurisdiction of the Bureau of Forestry, Minerals Section.

Walker's (PADER, 1/19/79) preliminary conclusion was that the seep at Beach No. 7 was due to the presence of an old unplugged well through which hydrogen sulfide, sulfurous water, and salt water were escaping from subsurface formations. The actual well site was at that time paved over, and Walker (PADER, 1/19/87) correctly noted that the City of Erie No. 1 Presque Isle well (referred to in this and other documents as the "Beach No. 7 well") had been plotted in the wrong location on Pennsylvania Geologic Survey maps. Walker (PADER, 1/19/79) correctly surmised that this well was actually located at Beach No. 7, largely



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because (1) the seep area did not freeze over during the winter, (2) the area of bubbling gas was highly localized, (3) the colloidal nature of black particulate in the fluid, and (4) the fact that high formation pressures and hydrogen sulfide-bearing brines occurred in the Lockport dolomite. This memo also raised the possibility that the Hammermill injection fluids may have been escaping from the Bass Island Formation (Walker-PADER, 1/19/79).

PADER sampled the seep on February 21, 1979, and in addition to the expected high concentrations of iron (925 milligrams per liter (mg/l)) and hydrogen sulfide (10/mg/l), Walker (PADER, 3/2/79a) noted that ammonia was present at levels believed to be anomalously high (532 mg/l). He suggested that this anomaly might be related to Hammermill's injected pulping wastes, and that the seep be sampled for lignosulfonates. Further, he suggested that the injected wastes could have escaped the disposal reservoir via unplugged wells or fractures and might contaminate fresh water zones (Walker-PADER, 3/2/79a). Walker (PADER, 3/2/79b) also contacted the oil and gas inspector to obtain estimates for plugging the Beach No. 7 well.

### 3.5 Beach No. 7 Well Discovery and Subsequent Investigation (March 1979-April 1979)

Arrangements were made to uncover the well so that estimates of the types and rates of flow of the fluids could be obtained (Walker-PADER, 3/9/79). Preliminary estimates of the costs to clean out and plug the well were between $10,000 and $100,000 (Walker-PADER, 3/9/79). The well was uncovered by using a backhoe on March 21, 1979, and samples from the seep and the well bore were taken and submitted for analysis of lignosulfonate, chloride, methane, pH, and other parameters (Walker-PADER, 3/22/79). The well itself consisted of three strings of casing, a 3-inch casing surrounded by 6 1/4-inch casing inside of an 8 5/8-inch outer casing. The 3-inch a: i 6 1/4-inch casings had been plugged, and sulfurous water and hydrogen sulfide gas were escaping from between the 6 1/4-inch casing and the 8 5/8-inch casing (Walker-PADER, 3/23/79). A temporary cap with a "bleed-off valve" was installed until the well could be plugged (Walker-PADER, 3/23/79).

The fluid flow from the outer annulus of the Beach No. 7 well, and the depths at which the casings were set led Walker (PADER, 3/26/79) to correctly conclude that the seep was the result of the escape of formation fluids from the Bass Island dolomite up the outside of the 6 1/4-inch casing. Furthermore, he formalized his hypothesis (see Figure 3-2) that the Hammermill injection program was the cause of the seep (Walker-PADER, 3/26/79). Initial flow measurements indicated a 411.36 -gallon-per-day (gpd) flow rate (Walker-PADER, 4/5/79).

Walker (PADER, 4/12/79) further refined this hypothesis in a memorandum following the receipt of analytical results from the second round of sampling conducted on March 22, 1979. These results showed that "abnormally high amounts of ammonia (400 and 506 mg/l), boron (470 and 400 mg/l), and titanium (750 and 1,000 mg/l) not naturally found" in the ground waters of the area were present in the seep and well samples, respectively. Walker felt that the presence of these compounds indicated that Hammermill's spent pulping liquor was present in the samples, because these substances are widely used in the paper industry (Walker-PADER, 4/12/79). Lignosulfonates were not detected, and methane was detected at low (<0.4 ppm) levels (Walker-PADER, 4/12/79).

Walker's evaluation at this point (PADER, 4/12/79) is flawed on two levels:

1. The criterion of comparison should have been the presence or absence of these compounds in oil field brines, not in ground water.

2. These compounds are additives used in paper finishing, as indicated by the document Walker appended to this memo (PADER, 4/12/79).

The pulping liquor wastes were intercepted directly from the digestors and, therefore, did not include additives or paper filler materials (Brown and Spalding-HML, 12/66; Brown-HML, 3/26/81; and D'Appolonia/IT-HML, 10/27/83). In all fairness to Walker, he had not discovered the Brown and Spalding (HML, 12/66) article yet, and this was Walker's first formal presentation of his hypothesis.

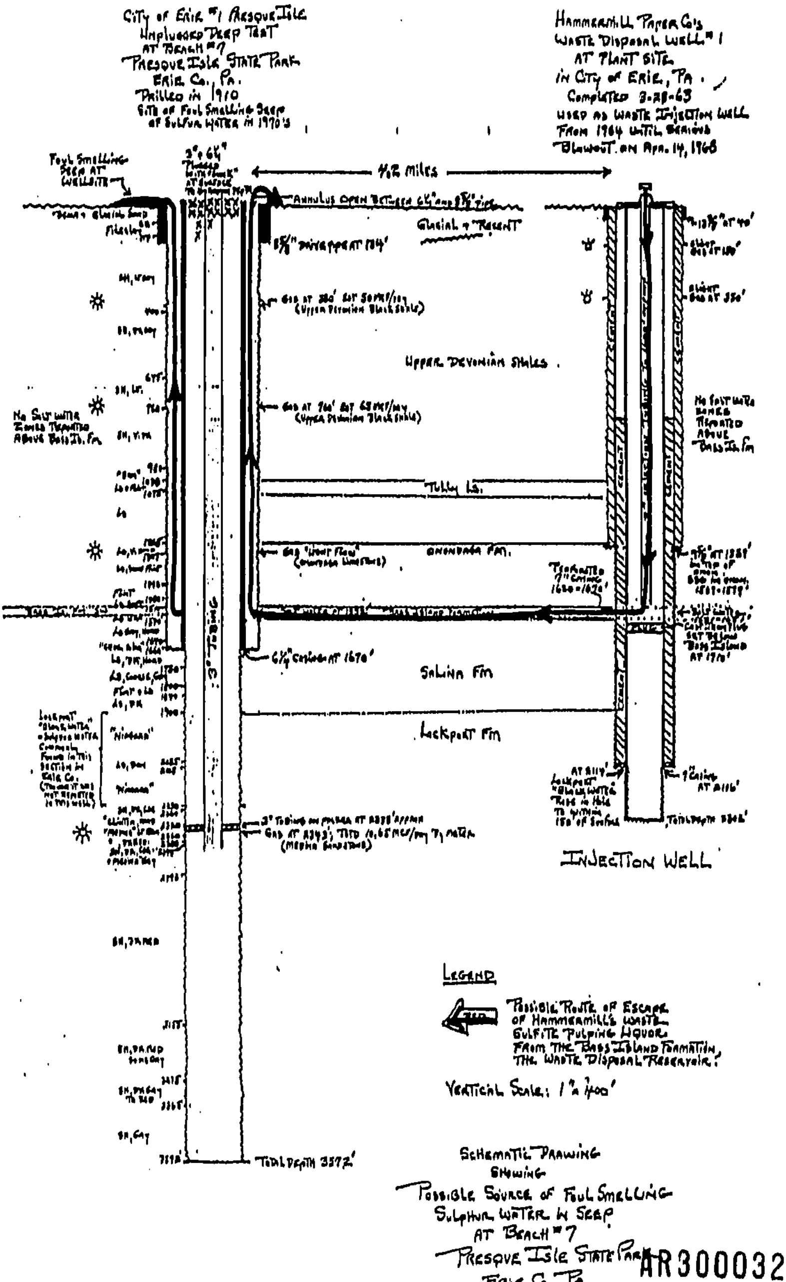


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FIGURE 3-2
PADER (WALKER-PADER, 3/26/79) HYPOTHESIS ON SOURCE
OF FLUID DISCHARGE FROM BEACH NO. 7 WELL

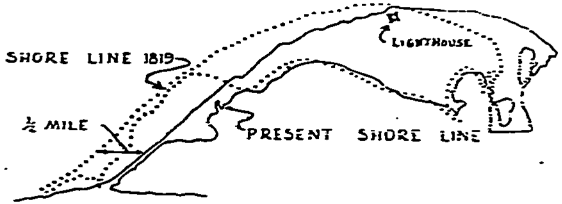
Walker (PADER, 4/12/79) stated that the seep area "has been a wet spot for years and been particularly foul smelling only in recent years." He reasoned that because the injected brine would have first displaced the normal connate water present in the Bass Island Formation, odoriferous brine containing pulping liquor would not have reached the well until the nonodorous connate brines were first displaced. That was the reason the seep had not drawn more attention in the early 1970s. Walker (PADER, 4/12/79) also noted the problems that the large number of older (and probably improperly plugged) oil and gas wells in Erie County might potentially present (by serving as conduits for the escape of brine/pulping liquor from the disposal reservoir).

Walker (PADER, 4/12/79) was also highly critical of the high injection pressures that Hammermill used in its injection program (1150 - 1250 psi, as subsequently reported in D'Appolonia/IT-HML, 3/83), because most porous rock will fracture at pressure of 1 psi per foot of depth or less. Such pressures, he felt, would further channelize the formation, causing the injected wastes to move more rapidly in one direction than in another due to "directional permeability" (Walker-PADER, 4/12/79). Walker mentioned that an effluent was sighted east of the gas well in Presque Isle Bay, and he was concerned that fluids might be rising around the outer 8 5/8-inch casing. Therefore, the temporary cap was left open to prevent a pressure buildup (Walker-PADER, 4/12/79). This action allowed fluids to continue to flow from the exposed well bore.

James Peace, a park engineer, reported that several old gas wells were located on Presque Isle near Beach No. 1 (to provide natural gas to heat cottages) and that at some of these "shallow gas wells," bubbles of gas could be seen coming up through lake water just offshore in Lake Erie (Walker-PADER, 4/20/79a). Over the past 100 years, the Presque Isle peninsula has moved approximately 1/2 mile to the east as a result of wave action (Jennings, undated, Figure 3-3). Mr. Peace further reported that an 18-hour shut-in test had shown a buildup of pressure to 30 psi at the wellhead (Walker-PADER, 4/20/79b).

The history of Presque Isle begins about 10,000 years ago, when the ice-front of the last ice age had melted back far enough to open the Niagara River outlet and let the impounded waters down to the level of our present Lake Erie. Since then the original shore of the Lake has been cut back to where, in the vicinity of Erie, it forms bluffs 60 feet high or more. During this process enormous quantities of earth have fallen to the mercy of the Lake where the material has been sorted out by the waves and some of the sand and pebbles deposited along the water's edge to form a beach.

Driven by the prevailingly westerly winds and storms the waves dash up the beach in a diagonal direction and, washing diagonally back, they carry along with them pebbles and sand, each time a little farther to the east. Distinctively colored pebbles can be watched as they are thus carried in and out, and, at the rate they often travel, they might go the entire length of the peninsula in a couple of days. Having reached the end of the peninsula such beach material is partly carried by storm waves on out into the deeper water while some of it finds its way around the end of the peninsula building up the beach in a more or less sweeping curve. At the southern end of this beach a hook or recurved bar often develops which sometimes more or less encloses a rounded pond or bay.




Peninsula has moved approximately one half mile east in the past one hundred years.

FIGURE 3-3
GEOMORPHIC CHANGES IN PRESQUE ISLE OVER THE LAST 100 YEARS
(Jennings, Undated)

On April 18, 1979, a meeting was held at the PADER regional offices in Meadville to discuss the Beach No. 7 well at Presque Isle with the Bureau of Water Quality and Erie County Department of Health and to discuss the potential impacts on the surrounding ground water (Walker-PADER, 4/23/79a). Mr. Saylor stated that the seep had an unpleasant odor in the early 1970s when he had visited the site, and Mr. Peace noted that the odor from the seep had become much worse during the previous 2 years (Walker-PADER, 4/23/79a).

### 3.6 First Meeting with Hammermill (April 1979)

On April 19, 1979, PADER officials met with Hammermill representatives to discuss the "possible source of industrial wastes flowing from the old, unplugged well at Beach No. 7" (Walker-PADER, 4/23/79b). Walker (PADER, 4/23/79b) reviewed the available chemical and geologic evidence and told Hammermill that it was their judgment that the pulping wastes injected during 1964-1972 were flowing from the Beach No. 7 well.

Walker stated that Hammermill initially denied that titanium dioxide and paper filler materials were ever injected into the subsurface, but "reversed themselves" when he read a passage in "Dr. Brown's 1966" article that "clearly stated that Hammermill's spent pulping liquor contained . . . paper filler materials such as . . . titanium dioxide . . ." (Walker-PADER, 4/23/79b). At this point, Walker was clearly in possession of the Brown and Spalding (HML-12/66) article, but he had not read it in its entirety and was quoting the article out of context (see Section 3.1 of this report).

Hammermill agreed to meet with PADER again after it had a chance to become familiar with the technical aspects of the problem (Walker-PADER, 4/23/79b).

### 3.7 Further PADER Investigations (April 1979-June 1979)

PADER conducted a 7-day shut-in test of the Beach No. 7 well, and it recorded a stabilized pressure of 31 psi and a flow rate after shut-in of

360-411 gpd (Walker-PADER, 4/27/79). Walker (PADER, 4/27/79) comments that this pressure is sufficient to support a column of water 76-feet high and that a considerable amount of sulfurous water should be expected to flow to the surface during plugging operations. An important technical note is appropriate at this point: Shut-in pressures at the wellhead are the result of the combined effects of gas pressure from the overlying Devonian shales and hydrogen sulfide exsolved from formation fluids surrounding the borehole, as well as pressures from the liquid phase. Walker's comment must be treated as a qualitative statement provided to add emphasis. Following the pressure tests the well was left open to prevent a pressure buildup (Walker-PADER, 5/2/79).

Additional analytical testing by PADER's Harrisburg laboratory indicated that samples contained high levels of nickel (5.95 mg/l), boron (470 mg/l), titanium (1 mg/l), and ammonia (532 mg/l), which Walker (PADER, 5/10/79) attributed to paper fillers and coatings. Walker persisted in his belief that paper fillers and additives were injected into the subsurface. By this point, Hammermill had hired Mr. Carl Burgchardt, a certified professional geologist, for assistance (Walker-PADER, 5/7/79).

During the PADER investigations at Beach No. 7, dead trees were noted. Mr. Woodrow Colbert was assigned to determine the cause of the tree kills within the park, and he called Walker for a briefing. During the briefing, it was noted that a 6- to 9-foot rise in the level of Lake Erie may have been a factor in the death of the trees (Walker-PADER, 5/11/79).

### 3.8 Second Meeting Between Hammermill and PADER (May-June 1979)

Hammermill presented its rebuttal to the earlier PADER allegations which included the following responses:

1. Injected wastes caused compression of the connate brines that had a "negligible (pressure) effect" on the Beach No. 7 well.

2. Boron and titanium could be naturally occurring.

3. The fluid at the Beach No. 7 well had such a high chloride content that it could not be injected wastes, because wastes would have diluted the brine.

4. Wellhead pressures could be the result of gas pressure.

5. Lockport brines could have corroded the well casing, resulting in the fluid flowing to the surface at Beach No. 7 (Walker-PADER, 5/2/79).

Walker (PADER, 5/2/79) strongly disagreed with the last point based on observed pH measurements, the fact that the Bass Island Formation is a carbonate, and the condition of the casing at the surface.

Internal Hammermill documents obtained by Versar during this investigation indicate that their calculations show that the pressure gradient would have caused the connate brines within the Bass Island Formation fluids to flow at the Beach No. 7, but Hammermill's consultant concluded that the flow would not be composed of injected wastes (Burgchardt, 5/31/79).

Analyses of the fluid samples from the Beach No. 7 well obtained on May 2, 1979, by PADER which showed the presence of tannin/lignin (27 mg/l), were also presented to Hammermill representatives (Walker-PADER, 5/31/79). Hammermill agreed to supply a written report to PADER summarizing the technical information that was discussed during this meeting.

Hammermill internal correspondence obtained by Versar indicates that they originally believed it was possible that the injection program could have caused the flow of a natural brine from the well (Brown-HML, 6/19/79). However, they felt that because the wells were operated and plugged under proper state permits, it was the state's responsibility to plug the leaking Beach No. 7 well (Brown-HML, 6/19/79).

3.9 <u>Initial Hammermill Report, PADER Criticism (July-August 1979)</u>

Hammermill's consultants submitted a letter report (D'Appolonia/IT-HML, 7/19/79) that discussed the points made during the May 29, 1979, meeting and contained the following conclusions:

1. The 50-foot injection interval assumptions used in the original Dow (HML, 11/11/62) feasibility study were unrealistic.

2. The seep at Beach No. 7 is a mixture of Lockport brines and other naturally occurring brines that have escaped their reservoirs because of deteriorating packers and casings.

3. The injection liquor contained no titanium, boron, or ammonia, and many of these substances are common in evaporite deposits such as the Salina Formation which underlies the Bass Island dolomite.

4. Low flow values for Bass Island Formation fluids observed during the development of Hammermill well 3 indicate that the disposal reservoir behavior was not one of compression, but rather injected fluids migrated laterally. This was a reversal of an earlier position (see Walker-PADER, 5/2/79).

5. The low flow values at Hammermill well 3, which is located only 450 feet away from the nearest injection well, precluded the possibility that similar surficial flows of subsurface brines would be observed at the Beach No. 7 well located 4.5 miles away.

The finite element computer simulation contained in this report was developed by using the known injection rates for the three injection wells and monitoring pressure buildups, and substituting variables for hydrogeologic parameters until the variables resulted in a solution that closely approximated the field conditions observed at Hammermill well 3 (D'Appolonia/IT-HML, 7/19/79). Then these hydrologic parameters and the injection history of the wells (history during 1964-1971) were used to model the rate of pressure buildup and decline until 1978. The modeled pressure at Presque Isle would never have exceeded 300 psi and would have declined rapidly thereafter to near zero by 1978 (D'Appolonia/IT-HML, 7/19/79).

Versar questions the basic assumption that the fluid flow rate can be used to establish whether the reservoir behavior results from compression or displacement of connate brines; both processes are probably involved. Furthermore, as PADER noted, the rate of flow at Hammermill well 3 only indicates that there was sufficient head to bring the fluid to the surface (Westlund-PADER, 8/23/79). The flow rate is

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also a function of porosity and permeability, not exclusively fluid pressure. If two reservoirs have identical formation pressures and porosities, but one has low permeability and the other has high permeability, then wells installed in each reservoir will have different flow rates, but both will equilibrate to exactly the same static water level. The well in the low-permeability formation will simply take longer to equilibrate.

The model contained in the D'Appolonia/IT report (HML, 7/19/79) hinges its estimate of pressure at the Beach No. 7 well on the hydrologic parameters developed by using a figure of 670 psi for Hammermill well 3. However, the figure of 670 psi for the pressure at Hammermill well 3 is only the minimum pressure at that well. Therefore, the model can only conclude that the Beach No. 7 well experienced a minimum rise of 300 psi in pressure; higher values are possible.

The 300 psi minimum rise would be in addition to the normal hydrostatic pressure in the formation. This is particularly important, because D'Appolonia (HML, 3/83) contends later that the Bass Island Formation is already under considerable artesian pressure naturally. Therefore, depending on the natural hydrostatic level in the Bass Island Formation, the Hammermill injection program could have forced a naturally occurring fluid from the formation.

### 3.10 PADER Investigations and Negotiations with Hammermill (July 1979-October 1979)

Walker visited the site on July 26, 1979, with other PADER representatives and collected more samples, which were split with Hammermill for laboratory analysis. Analyses detected ammonia (490 mg/l), titanium (12.1 mg/l), boron (137 mg/l), and tannin-lignin (132 mg/l). The well was still seeping sulfurous water onto the ground (Walker-PADER, 8/15/79 and 8/17/79). As a result, Carlyle Westlund, hydrogeologist for PADER, recommended that the Bureau of Water Quality Management require Hammermill to plug the well and to assess the impact of the Beach No. 7 well, and that PADER begin the preparation of a case against Hammermill (Westlund-PADER, 8/23/79).

PADER Secretary, Mr. Clifford Jones, had a breakfast meeting with one of Hammermill's vice presidents, Mr. James Stolley, and informally requested Hammermill's assistance in remedying the problems at Beach No. 7. Hammermill reiterated that based on their consultant's work, Hammermill felt that it was not responsible for the problems at Presque Isle. However, it was their policy to remedy any problem created by their operations when a reasonable cause and effect relationship could be shown (Stolley, 9/10/79). Hammermill stated that there were many abandoned gas wells in the area and that it might create future problems for them to take an action that would imply their injection program was responsible for the seepage. (Stolley-HMC, 9/18/79). Hammermill had not heard any comments refuting their consultant's report (Stolley, 9/10/79).

Previously unreleased Hammermill internal documents indicate that Secretary Jones was primarily interested in getting the well plugged (Stolley-HML, 9/7/79). Further, the memorandum suggests that Ken Young, Chief of the Water Quality group in PADER's Meadville office, felt that the D'Appolonia report suggests that the Hammermill injection program was not involved in the Presque Isle problem (Stolley-HML, 9/7/79). Another internal memo indicates that Hammermill informed Mr. Zinn, Regional Director of PADER's Meadville office, that if their consultants report indicated that it was Hammermill's problem, they would fix it, and if not, PADER should convince his people (D'Appolonia) they were wrong (Andrews-HML, 9/12/79).

The PADER Meadville office was reluctant to issue an order to Hammermill; Ken Young and James Erb wanted to get more evidence first (Walker-PADER, 9/19/79). PADER's environmental management section had earlier recommended that ground-water samples be obtained to determine whether contaminants from the well were spreading in the water table (Lesher-PADER, 9/11/79).

Secretary Jones responded to Hammermill's September 10, 1979, letter, stating that PADER believed that a reasonable cause and effect relationship did exist and that the Meadville office was arranging a meeting to further discuss the technical aspects of the problem (Jones-PADER, 9/26/79). John Walker's (PADER, 10/5/79) telephone memorandum indicates that Mr. Westlund had contacted EPA Region III and that EPA was interested, but PADER was not yet ready to request their help.

3.11 Technical Meeting Between Hammermill and PADER (October 1979)

At the October 11 meeting, Mr. William Hellier of PADER presented the rationale for explaining how the pressure buildup from the Hammermill injection well could have caused the seep at Beach No. 7 based on the Hagen-Pouiselle equation for laminar flow (Walker-PADER, 10/11/79). This application of this equation is improper for a number of reasons that will be discussed at length in Section 6.0 of this report. PADER also produced a fracture trace map prepared by the U.S. Department of Energy indicating that a lineament passed through the Hammermill plant in the general direction of Presque Isle (Andrews-HML, 10/18/79).

Hammermill began to suspect that the tests for tannin-lignin were unreliable. Hammermill internal correspondence indicates that test reagents produced a massive precipitate that had to be filtered out, and this may have induced error. Also, reducing agents such as ferrous iron resulted in interference (McMillen-HML, 10/10/79).

3.12 PADER Involves the USGS (October-December 1979)

PADER Bureau of Parks secured the assistance of the U.S. Geological Survey (USGS) to assist in the collection of ground-water samples to determine if the flow of contaminants had contributed to the widespread death of trees within the park (Walker-PADER, 10/22/79). Mr. David Click of USGS suggested that samples be obtained at depths of 70-90 feet because he was concerned about the large areas of private land and water that might be affected. The state Bureau of Parks was only concerned with the upper water table (Forrey-PADER, 10/26/79). Mr. Young, Mr. Zinn, and Mr. Erb of PADER's Meadville office had attended a meeting with Hammermill officials on October 26, 1979, and reported that there was a good chance Hammermill would plug the well or pay for most of it.

The USGS performed its preliminary investigation and submitted its proposal (Walker-PADER, 11/20/79). Shortly thereafter, PADER received new analytical results for brine samples from the Beach No. 7 well analyzed by Monsanto Research Corporation (Walker-PADER, 11/20/79). The results showed the presence of diethyl phthalate (130 ug/l), di-n-butyl phthalate (8.8 ug/l), anthracene and/or phenanthrene (9.6 ug/l), and fluoranthrene (18.0 ug/l). Walker (PADER-11/20/79) notes that these are plasticizers and dyes used in paper-making. Plasticizers and dyes are additives and, therefore, would not have been present in the pulping liquor.

Walker suggested that the Beach No. 7 well should not be capped, because that might cause a pressure buildup, causing other wells in the area to begin to flow (Walker-PADER, 11/27/79a). This logic is specious; any well where the hydrostatic head of the Bass Island fluid is above the surface would already have been flowing, and capping the Beach No. 7 well should not have materially affected other wells. Walker also wrote that over 100,000 gallons of foul-smelling, chemically laden fluids had entered the ground water at Beach No. 7 since March 1979 when PADER first became aware of the problem (Walker-PADER, 11/27/79c).

Negotiations with Hammermill were still in progress on November 30, 1979 (Forrey-PADER, 12/4/79).

### 3.13 USGS Proposal to Study Ground-Water Contamination (February-March 1980)

USGS submitted its proposal and the results of its analyses of samples from the Beach No. 7 well on February 8, 1980. These were the first extensive analytical results obtained, and they showed at least two priority pollutants, cadmium (800 mg/l) and lead (6,000 mg/l), at levels exceeding the federal water quality criteria (Click-USGS, 2/8/80). Organics were also present, including 2-3-5 trimethyl hexane, 1-4

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dimethyl benzene (1-2 ug/l), and anthracene or phenanthrene (1-2 ug/l) (Click-USGS, 2/8/80). The USGS proposal estimated that the investigation would cost $100,000 and would take 324 days to complete (Click-USGS, 2/8/80).

Secretary Jones held a meeting regarding the USGS proposal and the problems created by the Beach No. 7 well and its continued flow. Secretary Jones ordered that the well be plugged by using oil and gas monies. Secretary Jones informed Hammermill that it would be held liable for any damages caused by its wastes and that he expected the U.S. EPA would become involved through the USGS (Walker-PADER, 3/13/80).

Hammermill internal correspondence indicates that it had become aware of the USGS proposal, but it was still proceeding with a plan to make a contribution and was working out the legal details toward a settlement agreement (Brown-HML, 3/17/80).

### 3.14 PADER Moves Toward Plugging the Beach No. 7 Well (March-April 1980)

PADER officials met to discuss Hammermill's contribution to lay the groundwork for plugging the well on March 19, 1980, including the preparation of plugging specifications and press releases, and to discuss the need for further research on tree mortality, soil contamination, and sampling at the Beach No. 7 well and at the abandoned water wells near the lighthouse and the park superintendent's house (Walker-PADER, 3/21/80). Walker became concerned that "PADER should not be put in the position of plugging the well too soon and thereby covering up vital facts and evidence which may be needed later" (Walker-PADER, 3/25/80). Walker (PADER, 3/25/80) recommended that the well simply be shut-in to allow time for further investigations; he felt that federal agencies would soon become involved, because the USGS felt that the ground water over large areas might be endangered. This is a reversal of PADER's earlier position, that the well should not be capped.

PADER decided to shut in the well until the 1980 park season concluded (Walker-PADER, 3/31/80). Walker (PADER, 4/1/80a) also forwarded a copy of analyses by Monsanto Research Corporation to Mr. Forrey, Director of the Bureau of State Parks, indicating that in addition to the previously discussed compounds, the samples also contained abietic acid (8.9 ug/l) and dehydroabietic acid (3.1 ug/l). Walker (PADER, 4/1/80a) attributed the presence of these compounds to paper additives, namely, sizing and printing inks. Walker also prepared a request for estimates by an independent laboratory for 16 inorganics and 113 priority pollutants for use in future litigation (Walker-PADER, 4/1/80b).

### 3.15 Initial Press Coverage (April-May 1980)

A reporter was dispatched to Presque Isle in response to a visitor's complaint (Walker-PADER, 4/11/80). An ensuing newspaper article mentions Hammermill's potential responsibility for the discharge. Nevertheless, Hammermill met with Mr. Zinn of PADER's Meadville office and offered to pay up to $25,000 on an equal-payment basis to plug the well.

In response to inquiries, PADER prepared a press release (Walker-PADER, 4/11/80) and immediately capped the Beach No. 7 well (Walker-PADER, 4/14/80). Other than during the short period when the well was shut in for pressure testing, the well had been allowed to flow out onto the ground since its discovery.

### 3.16 Site Cleanup and Further PADER Activities (April-May 1980)

PADER brought in clean sand to cover the area of blackened soil and removed the dead trees that were standing nearby (Walker-PADER, 4/21/80). Walker (PADER, 4/21/80) noted a hydrogen sulfide odor that surrounded the well after the well had been shut in, and he surmised that the cap was leaking slightly.

Secretary Jones wrote to the USGS and declined their proposal for a ground-water study based on a lack of funds to finance an extensive study such as the one proposed (Jones-PADER, 4/16/80). Instead, PADER contacted Roy F. Weston Inc. to evaluate soil contamination and cleanup at Beach No. 7 (Snyder-PADER, 4/15/80). Sampling of soil and shallow ground water was conducted by Weston and PADER by using a posthole digger, and these activities were filmed by a local television crew for the evening news (Walker-PADER, 4/25/80a).

Funds in the amount of $100,000 were officially committed to the plugging project and the restoration of Beach No. 7 (Sterner, 4/24/80). Shut-in pressures at the Beach No. 7 well had stabilized at 32-33 psi (Walker-PADER, 4/25/80b).

3.17 PADER Meets With Weston Consultants (May 1980)

On May 12, 1980, PADER personnel met with representatives of Roy F. Weston, Inc. to discuss the preliminary results of their investigation. The following statements are the preliminary conclusions:

1. The groundwater near the Beach No. 7 well was contaminated with high ammonia, chloride, and strontium concentrations in test holes drilled near the well.

2. Lake water analysis showed levels of ammonia and chloride higher than expected for background concentrations.

3. It was possible that fluids from the well were getting into the lake.

4. The fluid contains at least 14 priority pollutants and should be considered as potentially hazardous (Walker-PADER, 5/14/80).

Weston recommended that PADER (1) close Beach No. 7 until soil and ground-water samples could be obtained and tested for all 129 priority pollutants, (2) plug the well, taking care to gather all the information needed to understand and resolve the problem, (3) conduct an area-wide survey of other abandoned wells to determine if similar problems exist elsewhere, and (4) have a areal photography study, including infrared, to assess stress on vegetation (Walker-PADER, 5/14/80).

PADER chose to immediately undertake the additional ground-water sampling suggested by Weston. PADER requested that Weston provide analytical results by the date that Beach No. 7 was scheduled to be opened to the public, May 24, 1980 (Walker-PADER, 5/14/80).

3.18 PADER's Concern Over Tree Mortality Grows (May 1980)

Walker (PADER, 5/15/80) became concerned about the presence of high concentrations of lithium (1800 mg/l) in USGS samples from the Beach No. 7 well, and he believed that they do not appear to be the natural concentrations given by Poth (1962), as 0-219 mg/l for Pennsylvania brines. Further, Walker quotes USGS Water Supply Paper No. 1473 (1952) by stating that lithium is toxic to plants. Walker (PADER, 5/15/80) also cited a paper, saying that "lithium is relatively rare in the Earth's crust, being concentrated principally in granitic rocks." However, on the same page as the toxicity information, the USGS Water Supply Paper No. 1473 (1952) states that "lithium tends to be concentrated in evaporites," and Walker (PADER, 5/15/80) had underlined this passage in his own copy. This glaring omission is particularly disturbing, because the Bass Island Formation rests directly on top of the Salina evaporites, and his contention that the lithium concentrations "do not appear to be natural" (Walker-PADER, 5/15/80b) lacks merit.

Walker (PADER, 5/16/80) was also quite concerned over the levels of strontium observed at the Beach No. 7 well, noting that strontium is a pigment used in paper-making (a passage that he underlined in his memo). Walker noted that Spalding et al. (HML, 5/65) state that the pulping liquor contained paper filler materials from the mill water used to wash the pulp. However, as with the Brown and Spalding (HML, 12/66) paper that Walker cited earlier, Spalding et al. (HML, 5/65) state in the next paragraph that this wash water could not be used in the injection program. Walker failed to appreciate this distinction, took this section out of context, and appeared to persist in his incorrect belief that secondary, paper-finishing materials were injected.

### 3.19 PADER Moves Ahead With Plans to Plug the Beach No. 7 Well (May-July 1980)

In a May 19, 1980, meeting, PADER decided to plug the well as "expeditiously as possible" in a manner that would permit the gathering data on the types and depths of fluids entering the well bore (Walker-PADER, 5/21/80). Furthermore, PADER's chief counsel suggested that the USGS be notified so that it would have an opportunity to gather information (Walker-PADER, 5/21/80). At this point, PADER assigned two attorneys to the case (Walker-PADER, 5/23/80a).

Weston's analysis of ground water collected on May 15, 1980, at Beach No. 7 revealed the presence of 1-1-1-trichloroethane (<0.1 ppm), benzene (34 ug/l), toluene (26 ug/l), xylenes (22 ug/l), ethyl benzene (3.5 ug/l), and phenols (<1 ug/l) according to its preliminary results (Walker-PADER, 5/23/80b). However, Weston concluded that there were no adverse effects on the ground water that would prohibit the use of the beach (Snyder-PADER, 6/2/80).

During June 1980, PADER prepared bid documents and plugging specifications. Walker continued to be interested in the tree mortality on Presque Isle and its possible connection to the flow of wastes from the Beach No. 7 well. Walker conveyed these interests to a PADER attorney (Walker-PADER, 6/10/80). EPA was already planning to run a low-altitude infrared study over the Erie area in September 1980 that would yield usable information on the pattern of tree kills (Walker-PADER, 6/16/80).

Walker (PADER, 6/26/80) learned that the Bass Island brines were analyzed for lithium and strontium from Hammermill's 1964 permit application for injection well 2. He hypothesized that these were "marker constitutents" in the pulping wastes. He questioned why Hammermill would be analyzing for these parameters. A review of the analyses indicates that lithium chloride and strontium chloride were analyzed along with salts of potassium, calcium, magnesium, and sodium; apparently, Hammermill was trying to characterize the brine chemistry.

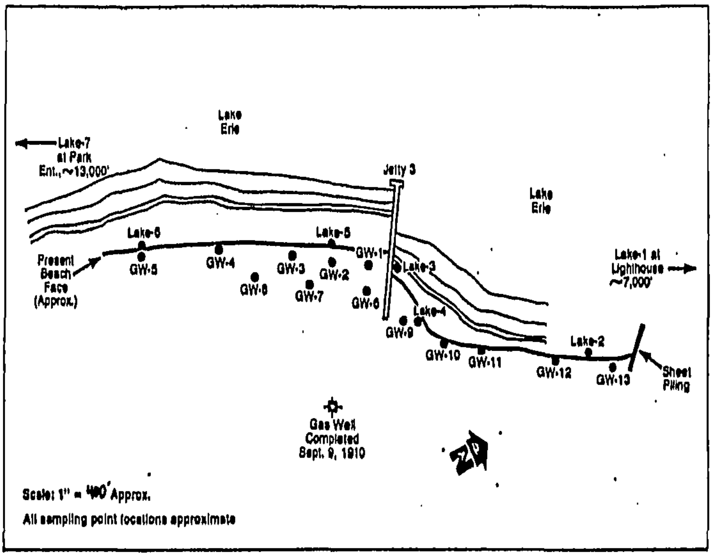
Walker (PADER, 7/1/80) also became concerned that radioactive wastes may have been injected. He based this concern on a 1970 letter from Hammermill requesting information from the State of Pennsylvania "for the purpose of establishing guidelines for the handling and disposal of radioactive materials at our divisions throughout the country." Walker (PADER, 7/1/80) requested that an analysis for radioactivity be included in the plans to sample at Beach No. 7 because he felt radioactive strontium may have been present in injected wastes.

Hammermill had the Birdwell Company run a radioactive tracer log to locate the leak in the casing following the blowout of Hammermill well 1 (PDOH, 4/15/68). This procedure consists of injecting a small amount (i.e., quarts) of radioactive material, which concentrates at the leak and can then be located with instruments. There is no indication in the correspondence that PADER was aware of this.

### 3.20 Weston Reports on Soil and Ground-Water Contamination (July 1980)

Weston (PADER, 7/1/80a) submitted its technical report on July 1, 1980, concluding that there was no significant influence of the well discharge on the ground water underlying the beach and that no imminent health hazard existed within 100 feet of the water line at Beach No. 7 (See Figure 3-4). Weston (PADER, 7/1/80a) also concluded that because the fluid from the well was 25 percent heavier than water, it would be expected to travel faster vertically than laterally. There was no obvious pattern to the results which would indicate the well was the source of the lithium in the ground water (Weston-PADER, 7/1/80a). Lastly, boron and strontium values in the ground water were not appreciably different from those of the lake water (Weston-PADER, 7/1/80a).

A separate letter report discusses soil contamination and clean-up (Weston-PADER, 7/1/80b). Water samples from the Beach No. 7 well that were analyzed for priority pollutants showed high levels of inorganics,




PRESQUE ISLE BEACH NO. 7
SAMPLING LOCATIONS
MAY 15, 1980

| Groundwater Sampling Location | Groundwater Analysis Analyses $NH_3$-N mg/L | Cl mg/L | B mg/L | Sr mg/L | Li mg/L |
|---|---|---|---|---|---|
| 1 | 1.96 | 19.3 | 0.10 | 0.15 | 0.30 |
| 2 | 1.96 | 19.5 | <0.10 | 0.21 | 0.02 |
| 3 | 1.68 | 20.4 | <0.10 | 0.15 | 0.05 |
| 4 | 1.68 | 20.6 | <0.10 | 0.18 | 0.04 |
| 5 | 1.40 | 18.4 | <0.10 | 0.15 | 0.02 |
| 6 | 1.40 | 16.7 | <0.10 | 0.10 | 0.06 |
| 7 | 1.40 | 18.6 | <0.10 | 0.15 | 0.60 |
| 8 | 1.12 | 18.3 | 0.13 | 0.17 | 0.55 |
| 9 | 0.56 | 18.4 | 0.10 | 0.17 | 0.27 |
| 10 | 0.56 | 19.7 | <0.10 | 0.10 | 0.04 |
| 11 | 0.56 | 19.9 | <0.10 | 0.14 | 0.17 |
| 12 | 1.12 | 19.3 | <0.10 | 0.19 | 0.20 |
| 13 | 0.56 | 19.5 | <0.10 | 0.17 | 0.16 |
| **Lake Sampling Location** | | | | | |
| 1 | 0.28 | 20.0 | <0.10 | 0.13 | <0.02 |
| 2 | 0.84 | 20.6 | <0.10 | 0.13 | <0.02 |
| 3 | 0.84 | 20.2 | <0.10 | 0.13 | <0.02 |
| 4 | 0.28 | 20.0 | <0.10 | 0.15 | <0.02 |
| 5 | 0.28 | 20.6 | <0.10 | 0.17 | <0.02 |
| 6 | 1.12 | 20.7 | <0.10 | 0.26 | <0.02 |
| 7 | 0.84 | 22.7 | <0.10 | 0.17 | <0.02 |

FIGURE 3-4
PRESQUE ISLE BEACH NO. 7 SAMPLING LOCATIONS, AND
CHEMICAL ANALYSES OF GROUND WATER AND LAKE SAMPLES
(Sampling and Analyses by Weston-PADER, 7/1/80a)

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but organic contamination was quite low (Weston-PADER, 7/1/80a). Soil samples were taken from the Beach No. 7 well area (Figure 3-5). U.S. EPA acetic acid extraction procedures were performed on the soil sample that appeared to be the most heavily contaminated. Concentrations of contaminants in the soil extract (Figure 3-5) were considerably below the U.S. EPA criteria, and the soil would not be considered a hazardous waste based on inorganic constituents (Weston-PADER, 7/1/80b). Weston (PADER, 7/1/80b) did not specifically test for organics in the soil, but they felt that the low levels of organics in the well discharge indicated that organics would probably not be retained by the soil. However, the soil then could be considered a hazardous waste under the U.S. EPA "de minimus" rule, according to Weston. The total volume of contaminated sand was estimated to be no more than 40 cubic yards (Weston-PADER, 7/1/80b).

Weston (PADER, 7/1/80b) reports several compounds from Beach No. 7 brine analyses that had not been previously known, including arsenic, selenium, thallium, 2 nitrophenol, 2-4 dimethylphenol, 4,6 dinitrocresol, and dioctyl phthalate at low levels (see Figure 3-5 for actual concentrations). Walker (PADER, 8/25/80) notes this and that the levels of lead, nickel, cyanide, phenol, benzene, and toluene were at concentrations significantly higher than in previous analyses. He attributes this to variability in the injection liquor which "certainly could not have been homogeneously constant, but would have varied from day-to-day and year-to-year" (Walker-PADER, 8/25/80). Walker did not consider laboratory variability to be a factor in the variations.

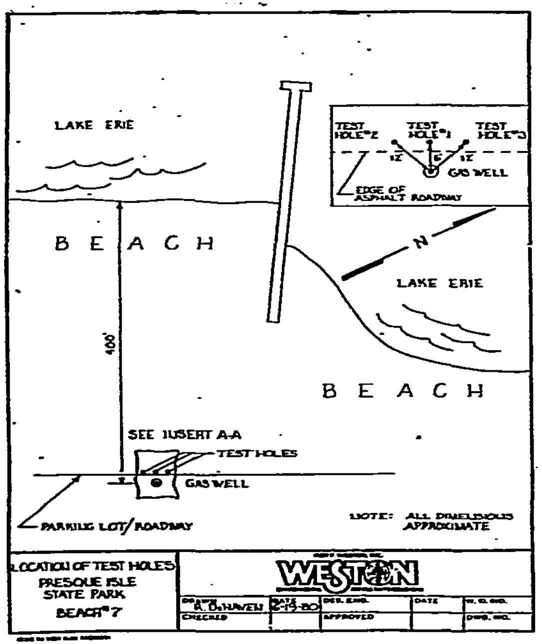
### 3.21 Increases in Shut-In Pressures, and Radiological Testing (August-September 1980)

PADER became increasingly interested in performing radiological tests to try to date the fluid discharge and to examine the extent of ground-water contamination (Walker-PADER, 8/26/80). The following tests were proposed: (1) a "gamma scan" to search for cesium-137, and (2) a destructive distillation test for tritium (from the fallout of nuclear testing in 1945). Strontium radioactivity tests were determined to be

Analysis of Presque Isle Abandoned Well Discharge for Priority Pollutants
Sample Taken May 15, 1980

| Parameter | May 15 Sample Concentration mg/L |
|---|---|
| Ammonia | 466 |
| Antimony | 4.0 |
| Arsenic | 16.0 |
| Barium | 6.3 |
| Beryllium | 0.09 |
| Boron | 63.0 |
| Cadmium | 0.57 |
| Chloride | 171,930 |
| Chromium | 0.40 |
| Cobalt | 2.17 |
| Copper | 0.67 |
| Iron | 89 |
| Lead | 9.0 |
| Lithium | 154 |
| Manganese | 0.81 |
| Mercury | .0015 |
| Nickel | 8.1 |
| Selenium | 12.0 |
| Silver | 0.50 |
| Strontium | 2,325 |
| Titanium | 3.0 |
| Thallium | 5.2 |
| Zinc | 0.56 |
| Cyanide | .03 |
| Phenol | .024 |
| 2-Nitrophenol | 1.0 a |
| 2,4-dimethylpheno | 0.8 a |
| 4,6-dinitro-O-cresol | 1.3 a |
| phenanthrene/ anthracene | 4 a |
| Dioctyl Phthalate | .065 |
| Benzene | .428 |
| Toluene | .139 |

a These values are in µg/L.




Analysis of Samples Collected 4/25/80
at Beach #7 Abandoned Gas Well, Presque Isle State Park

| | $NH_3$-N | Pb | Cr | Se | Ba | Cd | Cl | Sr | Cu | As |
|---|---|---|---|---|---|---|---|---|---|---|
| | All concentrations are in mg/l | | | | | | | | | |
| Groundwater Test Boring 1 | 88.2 | 0.94 | 0.08 | 0.48 | 1.0 | 0.14 | 26,680 | 438 | 0.14 | 0.375 |
| Groundwater Test Boring 2 | 106.9 | 1.19 | 0.11 | 0.38 | 1.0 | 0.18 | 37,220 | 654 | 0.16 | 0.500 |
| Groundwater Test Boring 3 | 18.2 | 0.33 | 0.02 | 0.35 | <0.2 | 0.04 | 6,354 | 102 | 0.03 | 0.073 |

FIGURE 3-5
LOCATION OF TEST HOLES AT PRESQUE ISLE STATE PARK, BEACH NO. 7, AND CHEMICAL ANALYSES OF GROUND WATER AND DISCHARGE FROM WELL
(Weston-PADER, 7/1/80b)

unwarranted. This plan hinged on the concept that the ground water would not contain any of these radioactive isotopes and that the formation waters are very old. So if detected, abnormally high levels of the isotopes in the surrounding vegetation would indicate that brines which seeped from the Beach No. 7 well were being taken up by root systems and were not naturally occurring (Walker-PADER, 8/26/80).

At about the same time, PADER became concerned, because shut-in pressures at the Beach No. 7 well had increased dramatically. The well pressure stabilized at 34-35 psi for 2 months, but began to rise in June, and it was 49 psi in late August (Walker-PADER, 8/27/80). PADER calculated that 56 psi would be sufficient to lift the casing from the hole if it was not properly seated and decided that the well should be vented if pressure rose to that level (Walker-PADER, 8/27/80).

The PADER legal staff completed its analysis of the relevant precedents surrounding liabilities from the plugging of the Beach No. 7 well. Chief Counsel Blazey recommended that PADER proceed immediately with plans to plug the well, to advise Hammermill, and to solicit Hammermill's comments (Blazey-PADER, 8/21/80).

Jack McCoy, USGS acting District Chief, contacted PADER personnel to inform them that matching funds had been allocated to the USGS proposed ground-water study in response to PADER's requests for assistance (McCoy-USGS, 8/22/80). The discussion during a meeting of PADER personnel concerned (1) the USGS proposal (which included surficial resistivity studies), (2) well plugging specifications, (3) a plan to locate all wells within a 5-mile radius, (4) a plan to collect water samples from water wells and fluid samples from the Bass Island Formation in wells drilled in the area, and (5) a decision to use EPA's laboratory in Cincinnati to analyze samples (Walker-PADER, 8/28/80). This was the first indication that the EPA would be involved in the project. Deputy Secretary Middendorf wrote back to the USGS that PADER had already conducted a limited ground-water study (Middendorf-USGS, 8/29/80).

A gamma scan for radioactivity conducted by PADER's radiological laboratory was negative. No cesium-137 was detected (the detection limit was 3.5 picocuries for a 5-day scan) (Walker-PADER, 9/2/80).

The wellhead pressure at the Beach No. 7 well continued to rise, and it reached 53 psi by September 8, 1980. PADER made plans to vent the well in the event that the pressure exceeded the 56-psi critical point (Westlund-PADER, 9/8/80).

### 3.22 Hammermill Withdraws Offer to Help Finance the Well Plugging (September 1980)

PADER prepared to advertise the bid for a well-drilling contractor to assist in plugging the Beach No. 7 well. At this point, Mr. Zinn, Regional Director of PADER's Meadville office, contacted Hammermill to solicit its participation in the plugging of the well (Zinn-PADER, 9/10/80). Zinn (PADER, 9/10/80) further mentioned that recent analyses indicated the presence of constituents not normally found in naturally occurring ground water.

### 3.23 PADER Starts Venting the Beach No. 7 Well to Relieve Pressure (September-October 1980)

On September 12, 1980, the pressure at the wellhead reached 56 psi, and PADER vented the well to relieve the pressure. Hydrogen sulfide gas escaped for 30 seconds, and black water flowed from the well for approximately 2 hours after opening the well (Westlund-PADER, 9/15/80). The well pressure built back up to 55 psi by October 3, 1980, and PADER again vented the well; following an initial release of hydrogen sulfide gas, black water flowed from the well at a rate of 432 gpd (Walker-PADER, 10/6/80).

### 3.24 PADER Investigates Possible Seep Near the Hammermill Well 3 (October 1980)

PADER received a complaint from a local citizen, Mr. Gene Hueser (10/6/80), who said that fluid was leaking from an area very near Hammermill injection well 3 (plugged). Notes written in the margin of this letter indicate that John Walker and Carlyle Westlund visited the site and found fluid that appeared to be oily, iron-rich, fairly clear and odorless. Walker's notes indicate that they determined it to be leachate from adjacent fill (Hueser, 10/6/80).

### 3.25 PADER and Hammermill Discuss Well Plugging Specifications (October 1980)

An October 15, 1980, meeting was held by PADER and Hammermill to discuss PADER's proposed specifications for the cleaning out, logging, testing, and plugging of the Beach No. 7 well (Walker-PADER, 10/20/80). Hammermill had only just received the plugging specifications, and it was not in a position to comment at that time. However, Hammermill indicated that it wished to collect split samples and sample other strata such as the Lockport Formation, that it felt might be involved (Walker-PADER, 10/20/80). Hammermill requested that all data be freely exchanged between both parties (Brosig-HML, 10/16/80).

Hammermill submitted its written comments on the plugging specifications and suggested that the testing program was primarily concerned with defining the influence of the Bass Island Formation on the seep, but it was vague about defining other possible influences (Andrews-HML, 10/28/80). In addition to numerous specific suggestions about gas and fluid flow measurements, Hammermill requested that PADER explicitly state the methods and types of analyses to be performed (Andrews-HML, 10/28/80).

### 3.26 Hammermill Makes New Offer to Underwrite Testing Program (October-November 1980)

Shortly after commenting on the the plugging and testing program, PADER Secretary Jones and other officials met with Hammermill's Dr. Brown (Brown-HML, 10/28/80). Hammermill reversed its recent decision to withdraw an offer to contribute to the costs of the well plugging project (Brown-HML, 11/14/80).

## 3.27 PADER Abandoned Oil and Gas Well Survey (December 1980)

An Erie County oil and gas inspector, Mr. Don Gaddess, made visual inspections of 87 oil and gas wells within a 5-mile radius of the Beach No. 7 well. Most were found to be buried or under buildings; those that could be found were in good shape, with no seeps or leaks observed or reported (Socolow-PADER, 12/18/80). People living in buildings that were constructed over the sites of these wells were questioned, and they reported no odors or seepages (Socolow-PADER, 12/18/80).

The Pennsylvania Topographic and Geologic Survey was looking for a drilling company that would allow them to sample the Bass Island brines (Socolow-PADER, 12/18/80).

## 3.28 PADER's Interest in Hydrogen Sulfide Grows (February-March 1981)

PADER's Air Quality Control personnel became interested in the composition of the gases escaping from the Beach No. 7 well and sampled the well on February 18, 1981. Samples indicated the presence of hydrogen sulfide (calculated to be 23,844 ppm) and large concentrations of methane (67.58-72.16 percent) (Walker-PADER, 2/19/81).

PADER sampled the gas flowing from the Beach No. 7 well again on March 19, 1981, with similar results (see Figure 3-6) for most of the gases, but hydrogen sulfide was at a considerably lower level (504.1-569.1 ppm) than the previous figure (Walker-PADER, 2/19/81), which was calculated based on saturated collection media (DeHaven-PADER, 6/11/81).

At this point, it is important to note that the levels found through these analyses reflect the concentrations of gases that accumulated during well shut-in (see Figure 3-6), so they should not be taken as indications of the ambient air conditions prevalent before the well was capped. The only clear and present danger would be to those venting the well, or looking to the future, to those near oil and gas rigs during drilling through the Bass Island Formation.

SUMMARY OF RESULTS

PRESQUE ISLE STATE PARK
BEACH NO. 7 WELL

Table I – Series One (Preliminary) 2/18/81

| Test # | $NH_3$ (PPM) | $H_2S$ (PPM) | CO (%) | $CO_2$ (%) | $O_2$ (%) | $N_2$ (%) | $CH_4$ (%) | [illegible] (%) | [illegible] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1-A | | | N.D. | N.D. | 2.9 | 17.6 | 67.6 | 9.1 | 2.8 |
| 1-B | Not Analyzed | | | | | | | | |
| 1-C | Not Analyzed | | | | | | | | |
| 1-D | | | N.D. | N.D. | 2.0 | 13.5 | 72.2 | 9.3 | 3.1 |

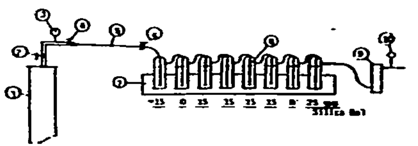
Table II – Series Two, 3/19/81

| Test # | $NH_3$ (PPM) | $H_2S$ (PPM) | CO (%) | $CO_2$ (%) | $O_2$ (%) | $N_2$ (%) | $CH_4$ (%) | [illegible] (%) | [illegible] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 2-A | | | N.D. | N.D. | N.D. | 4.0 | 81.3 | 11.5 | 3.2 |
| 2-B | N.D. | 504.1 | | | | | | | |
| 2-C | | | N.D. | N.D. | 1.3 | 10.9 | 75.0 | 10.4 | 2.5 |
| 2-D | N.D. | 569.1 | | | | | | | |
| Averages | | 536.6 | | | 1.6 | 11.5 | 74.0 | 10.1 | 2.9 |

N.D. – None detected
● Calculable Unknown – similar to Mercaptans in "City Gas"

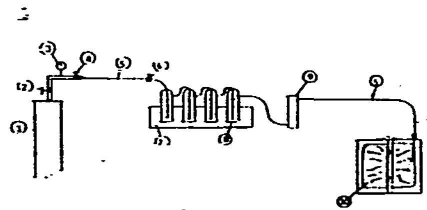
Test No. 1-B, 1-C SAMPLING APPARATUS Date 2-18-81

FIGURE II



Test No. 1-A, 1-B, 2-A SAMPLING APPARATUS Date 2-18-81

FIGURE I



2-B, 2-C, 2-D SAMPLING APPARATUS Date 3-19-81

FIGURE III

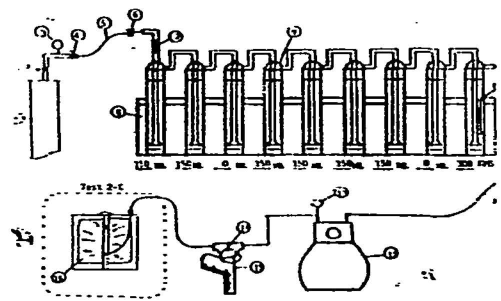



FIGURE 3-6
GAS SAMPLING APPARATUS AND ANALYSES OF SAMPLES
FROM PRESQUE ISLE BEACH NO. 7 WELL
(DeHaven-PADER, 6/11/81)

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3.29 PADER Requests Information on Hammermill Pulping Processes (February-March 1981)

PADER contacted Hammermill to brief the company on its efforts to secure a contractor to plug the Beach No. 7 well and to request that Hammermill voluntarily submit specific information on Hammermill paper processing, including (1) detailed information on chemical processes at the plant, (2) whether tannin-lignin was ever present in the spent pulping liquor, (3) descriptions of chemical process involved in bleaching operations, (4) a list of biocides and acids used in the injection program, and (5) copies of documents that support any of the above information (Duncan-PADER, 2/26/81).

PADER stated that it had received no bids on well plugging in response to their October 16 and December 19, 1980, offering (Duncan-PADER, 2/26/81).

Hammermill responded to PADER's request for process information by sending the documentation requested earlier. It is particularly important that Hammermill provided internal correspondence from 1964 and a copy of the Brown and Spalding's (12/66) article as evidence that mill water containing paper additives and fillers had not been injected, because preliminary testing indicated that it would render the injection system inoperable (Brown-HML, 3/26/81). Brown (HML, 3/26/11) noted that they believed the article had been quoted out of context during previous meetings with PADER representatives. Hammermill also acknowledged that tannin-lignin was present in the spent pulping liquor and provided a product data sheet for the biocide (Busan 881) the company had used (Brown-HML, 3/26/81).

PADER wrote another information request for (1) elemental chemical analysis of the byproduct wastes in the pulping process, (2) elemental chemical constituents and characteristics of the spent pulping liquor, and (3) information on whether any acids were used in association with the injection process and their chemistry (Weston-PADER, 7/21/81). Hammermill (Brown-HML, 8/25/81) responded with a brief description of the

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elemental chemistry of neutral sulfite pulping liquor garnered from the literature. The company noted that it was impossible for it to provide the detailed chemical analysis requested, because the process was no longer used, and no samples were available (see Section 3.1 of this paper).

3.30 Tree Mortality and "Black Inky Lineation" (December 1980-December 1982)

PADER became interested in a "large inky spot" in Lake Erie just off Presque Isle Channel and large areas of dead trees revealed by a November 11, 1980, EPA infrared study following a phone call to Ken Noble, an EPA photo interpreter (Walker-PADER, 12/17/80). PADER and EPA conducted a helicopter survey and ground-checked their areal observations. They concluded that (1) there was no current evidence that a phytotoxic chemical is actively stressing the trees on Presque Isle, (2) most tree dieback and mortality appears to be associated with low elevation and abnormally high water levels, (3) the dieback of cottonwood trees associated with the well site appears to be related to age (possibly to the presence of lithium), (4) to verify any possible relationship between tree mortality and the Beach No. 7 well would be expensive and time consuming, and (5) the large, black discolored area in Lake Erie appears to originate in a suspected fault line (see Figure 3-7), while a smaller chocolate-colored area is a point source (Nichols-PADER, 8/7/81). Donald Davis, a Penn State professor, was also present during this investigation; he agreed that most of the tree mortality was associated with low, wet areas, and the trees "were killed as a result of high water levels in the past, with or without toxic chemicals (Davis-PADER, 8/17/80).

The findings of Nichols (PADER, 8/7/81) are largely reiterated by Harmon (PADER, 8/11/80), who indicates that they were in possession of a "fracture trace map" at the time of the survey (Figure 3-7). Therefore, it is likely that Nichols' comment concerning the origin of the black lineations is based solely of the position of the discoloration. John

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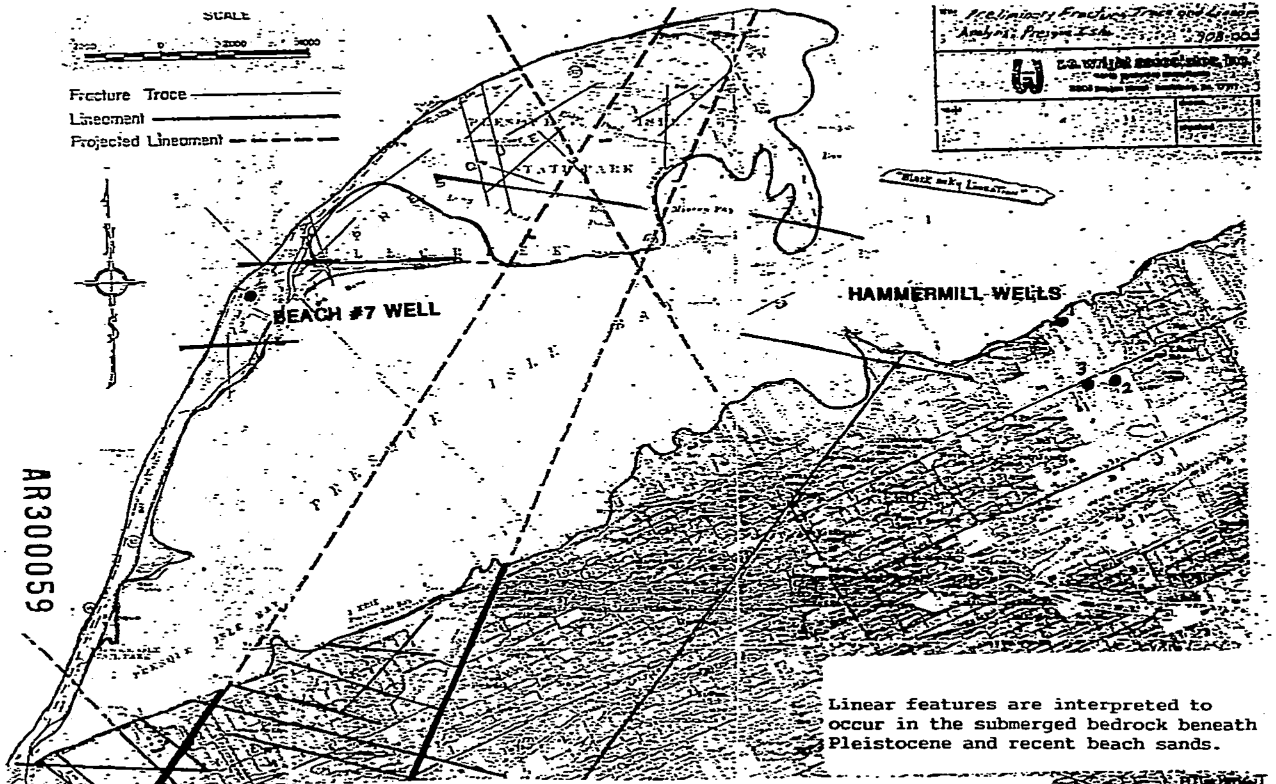


FIGURE 3-7
PRELIMINARY FRACTURE TRACE AND LINEAMENT ANALYSIS FOR PRESQUE ISLE
(Walker-PADER, 8/15/83)

Walker contacted Monsanto Research Corporation for further information on the black lineation. He was informed that it was not a continuation of any fracture trace that Monsanto had identified, but it was parallel to a high-density area of fracture traces that they had identified on land, and sampling would be required to determine the origin of the black lineation (Zeilinski, 8/31/81).

James Erb of the PADER Meadville office contacted John Walker and informed him that the black lineation was caused by discharge from the sewer line, that it changed shape with currents and lake conditions, and that the sewer line had been discharging sewage into the area since the early 1900s (Walker-PADER, 9/2/81).

A year later, EPA contacted Mr. Robert Wellington, an aquatic biologist for the Erie County Department of Health. Wellington also felt that the black lineation was the result of not only one leak but possibly as many as three leaks that they observed in the city sewer line (Wellington-DOH, 12/6/82). Furthermore, the city has a sewage discharge rate of 40 million gallons per day, resulting in a plume equal to the size of the black lineation (Wellington-DOH, 12/6/82). If the black lineation were the result of injected waste seeping from the subsurface, then at that rate of flow, all of the injection wastes would be exhausted in 2 months (Wellington-DOH, 12/6/82). In his opinion, if an injection well were seeping through a fracture beneath the lake, the area would probably be very small, not visible on the surface, and have very little effect on the lake compared with the effluent from city sewer plant (Wellington-DOH, 12/6/82).

John Walker felt that Mr. Wellington's logic was incorrect according to notes he makes at the bottom of this document (Wellington-DOH, 12/6/82). Walker felt that waste could be seeping out a fault and staining the lake bottom sediments, causing the lineation to be apparent when the lake was clear and the weather was good. Versar does not agree with this interpretation; the black material staining the ground at the Beach No. 7 well is more than likely iron sulfide precipitants created as the result of the acid environment of the well casing, concomitant with the release of hydrogen sulfide gas (D'Appolonia/IT-HML, 10/27/83). This reaction is well documented for Pennsylvania brines in Dresel and Rose (1985), a document that was produced independent of any Presque Isle investigation. Of course, iron might have been picked up from the overlying formations. However, Walker seems to be suggesting that the black material is characteristic of the pulping liquor, rather than a reaction product.

3.31 Early EPA Investigations: Field Investigation Team (FIT) Plume Study (October 1981-March 1982)

Ecology and Environment was assigned by U.S. EPA Region III the task of preparing a site inspection. Ecology and Environment personnel were the first EPA investigators appointed specifically to examine the Presque Isle site (Walker-PADER, 10/23/81). Ecology and Environment sampled the lake bottom sediment across the black lineation and reported its findings in an EPA FIT report dated March 23, 1982.

The FIT Report (Ecology and Environment-EPA, 3/23/82) states that its samples of the lake sediments indicated the presence of palmitic acids and esters, numerous alkanes, and very low levels of polynuclear aromatic hydrocarbons (PAHs). The available evidence neither supported nor refuted Walker's suggestion that the black lineation was the result of Hammermill pulping wastes escaping from the subsurface via fractures (Ecology and Environment-EPA, 3/23/82).

The FIT Report concludes that (1) the principal hazard at the Beach No. 7 well was to personnel involved in venting the hydrogen sulfide, (2) EPA locate and characterize other similar wells to evaluate the potential for more extensive discharges, and (3) if brines similar to the discharge at Beach No. 7 were responsible for the black lineation in Lake Erie, then the effect on aquatic life would be "devastating" (Ecology and Environment, 3/23/82). Additionally, the FIT Report provides a figure (Figure 3-8 of this report) showing that the black lineation is very close to the city sewer lines (Ecology and Environment-EPA, 3/23/82).

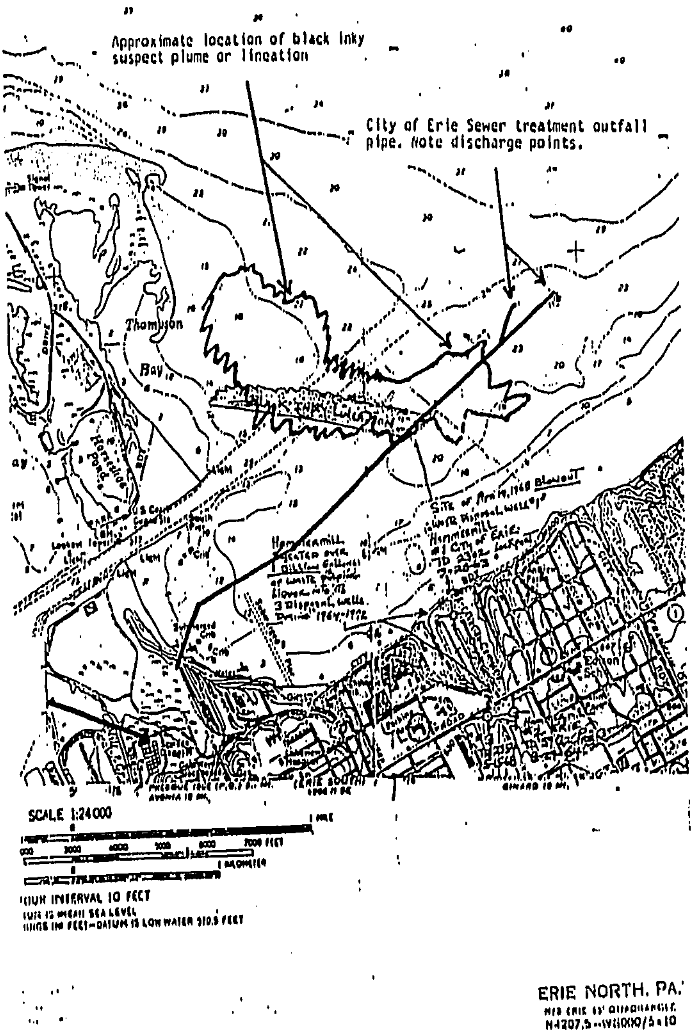


FIGURE 3-8
MAP SHOWING BLANK "INKY" SUSPECTED PLUME OR LINEATION
AND CITY OF ERIE SEWAGE LINE
(Ecology and Environment-EPA, 3/23/82)

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Samples from the Beach No. 7 well presented severe analytical problems which were caused by the formation of precipitates that prevented the analysis of base compounds (Austin-EPA, 12/30/81). Further, field blanks were found to be contaminated with high levels of toluene, casting a grave shadow over the toluene results and bringing into question the integrity of the entire sample set (Dreish-EPA, 12/15/81). Ecology and Environment (EPA, 3/23/82) made numerous suggestions for further refinements in sampling methodologies based on its experience at Beach No. 7.

### 3.32 Plans to Plug and Test Beach No. 7 Well Are Finalized (April-May 1982)

PADER met on April 2, 1982, to finalize its bid specifications, with EPA in attendance (Walker-PADER, 4/2/82). Westlund (PADER, 4/15/82) recommended that PADER attempt to plug the well before the summer park season began because of the continued rise in shut-in pressures at the wellhead. Westlund (PADER, 4/5/82) reasoned that the constant irritation of shutting in and venting the gases caused caving of material in the annulus and provided an easier avenue to flow.

PADER forwarded a copy of the final bid specifications to Hammermill (Westlund-PADER, 3/23/82) and to U.S. EPA Region III, which reviewed the specifications and concluded that, in addition to other comments, sampling protocols and procedures needed to be more clearly defined (Quirus-EPA, 5/24/82).

### 3.33 Full EPA Participation Begins in PADER's Investigations (April-July 1982)

Up until May 1982, EPA's investigations had been the result of their own interests in the the problems presented by the Beach No. 7 well at Presque Isle, and PADER had not made a formal request for assistance in its investigations. EPA met with PADER officials for the first time on April 21, 1982, to discuss concerns raised by the FIT Report (Ecology and Environment, 3/23/82) about widespread, even international, ground-water contamination from the flow of wastes through other abandoned oil and gas wells (Shoener-EPA, 5/4/82).

Shoener (EPA 5/4/82) recommended that to better understand the problem, the Field Investigation Team (FIT) should (1) review the plugging and testing specification to ensure that representative samples can be obtained, (2) recommend laboratory procedures, (3) conduct further areal photography of the Lake Erie plume, (4) locate and sample drinking water wells in the area, (5) attempt to chemically fingerprint the waste, (6) identify the areal extent and outcrops of the Bass Island Formation, (7) drill a background well in an uncontaminated area of the formation, (8) investigate the possibility of subcontracting a Penn State professor to examine tree mortality, (9) examine the need to conduct a broader geographic study, and (10) involve the USGS.

Following this meeting, as a result of reviewing the FIT report, Kleeman (EPA, 4/30/82) calculated the pressure buildup from Hammermill's injection wells based on the EPA guidance document "Radius of Pressure Influence from Injection Wells" (EPA-600/2-79-170). These calculations indicated that Hammermill's injection program could have caused enough pressure to induce flow at the Beach No. 7 well (Kleeman-EPA, 4/30/82). Chapter 6.5 discusses this model in more detail.

Following the receipt of the memoranda by Kleeman (EPA, 4/30/82) and Quirus (EPA, 5/24/82), EPA contacted PADER and offered agency assistance in the plugging and testing program at Presque Isle (Shoener-EPA, 6/7/82). In response, PADER formally requested that EPA assist in the collection and analysis of samples from the plugging and testing of the Beach No. 7 well (Weston-PADER, 6/18/82). In a meeting between PADER and EPA on June 18, 1982, both parties adopted the research agenda outlined originally by Mr. Shoener in May (Westlund-PADER, 7/12/82). EPA officially committed itself to supporting the PADER well plugging and testing program by developing a detailed sampling plan and an analytical program, by analyzing samples, and supplying personnel to aid in the sampling (Voltaggio-EPA, 7/16/82).

### 3.34 Final Plugging Preparations, EPA Investigation Begins (July-October 1982)

PADER advertised it final request for proposals, which were to be received by August 19, 1982, with the work to begin on September 20, 1982 (Early-PADER, 7/21/82). PADER accepted IPSCO as the plugging contractor. Plugging and testing were scheduled to begin on October 18, 1982, when EPA sampling teams and a trailer could be brought to the site (Walker-PADER, 9/17/82).

During the interim, a USGS literature search was initiated (Click-USGS, 8/25/82), and EPA provided a sampling plan for the investigation (Ecology and Environment-EPA, 8/6/82) and developed a list of compounds that would indicate the presence of pulping liquor in the samples. These "verification" compounds (Sloboda and Symms-EPA, 9/10/82) included:

| | |
|---|---|
| Resin Acids: | Abietic acid, dehydroabietic acid, isopimaric acid, 1-chlorodehydroabietic acid, pimaric acid, dichlordehydroabietic acid. |
| Phenolics: | Catechols, guicol, vanillin, syringaldehyde, acetosyringone, hydroxybenzaldehyde. |
| Chlorinated Phenolics: | Chlorinated phenols, chlorinated guicols, chlorinated vanillins, chlorinated catechols. |
| Fatty Acids: | Oleic acid, linoleic acid, linolenic acid, 9,10-epoxy stearic acid, palmitic acid. |

Sloboda and Symms (EPA, 9/10/82) also proposed special analyses for lignins. Nonchlorinated phenolics, lignins, and resin acids occur naturally in plants, but they probably would not persist long enough to be found deep underground along with ancient petroleum deposits or brine water sources. Strontium 90 and tritium analysis are useful indicators of man-made isotopes, but they were ruled out due to low-level occurrences, analytical difficulties, and detection limit problems (Sloboda and Symms-EPA, 9/10/82). Carbon 14 dating was considered to be a promising method to determine whether recent spent pulping brines were present (Sloboda and Symms-EPA, 9/10/82).

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Ken E. Davis Associates reviewed the plugging specifications, sampling plans, and other technical data, and they found the document to be technically acceptable, but the sampling techniques, equipment, and methods were not well addressed (Ken E. Davis Associates-EPA, 10/7/82).

Ken E. Davis Associates (EPA, 10/7/82) felt that (1) formations would surely be cross-contaminated after being connected by the borehole for 60 years, (2) the layer would probably not be pure waste but a mixture of brine and waste, and (3) if the purpose was to gather evidence for legal actions, they doubted that the data would be conclusive. Therefore, they recommended that it would probably more economical to plug the well from top to bottom with cement and to drill another well to determine the extent of contamination (Ken E. Davis Associates-EPA, 10/7/82). A similar suggestion was made by the Bureau of State Parks for safety reasons under a worst-case scenario of uncontrolled flow during plugging (Harmon-PADER, 8/5/82).

3.35 FIT Hazardous Ranking System Model (August 1982)

EPA revised the National Contingency Plan and established a Hazardous Ranking System (HRS) to establish national priorities for remedial action (Federal Register, Vol. 47, No. 137). An HRS score for the Presque Isle site was prepared. It lists hydrogen sulfide, cadmium, chromium, lead, boron, strontium, and lithium as the contaminants of concern (Ecology and Environment-EPA, 8/24/82) based on previous analyses by PADER. Lead was listed as the most toxic compound detected (Ecology and Environment-EPA, 8/24/82). The site scored high enough to make the National Priorities List (NPL) when the proposed rule was published in December 1982 (see Section 3.40).

3.36 Beach No. 7 Well Plugging and Testing (October-December 1982)

PADER issued press releases on October 8, 1982. The well was extensively tested, plugged with cement above the Bass Island Formation, and completed as a natural gas well between October 18 and November 17, 1982. Hammermill's consultants, D'Appolonia/IT, were onsite to collect split samples and to observe site operations. Extensive field notes and detailed fluid flow summaries are given in Walker's (PADER, 12/16/82) and IT Corporation's field notes obtained by Versar (Wright-HML, 11/16/82).

In addition to providing analytical samples, the formation tests also established that (1) the Bass Island Formation was the source of the black water in the 6-1/4 to 8-5/8 inch annulus and therefore was the source of the seep, (2) the Lockport Formation has sufficient hydrostatic pressure to flow to the surface , but its rate of flow was not great enough to cause flow to the surface overnight, (3) the flow rate from the annulus was not affected when the Lockport Formation was packered off or when the Lockport fluids were blown out. Therefore, movement of Lockport Formation fluid up the borehole did not contribute to the seep.

Several important observations were made after the Lockport Formation was cemented and the Bass Island Formation was packered off. On November 11, 1982, bubbles of gas were rising within the 3-1/2-inch packer casing. These bubbles ignited momentarily, and Draeger tube tests for hydrogen sulfide gas were negative (see page 98 of Walker-PADER (12/16/82) and page 146 of Wright-HML (11/16/82)). These observations support the existence of naturally occurring hydrocarbons in the Bass Island Formation.

Additionally, the failure of Draeger tube tests to detect hydrogen sulfide in the discharge through the 3 1/2 inch packer casing supports the argument that hydrogen sulfide gases observed at the seep were exsolved in the acidic environment surrounding the annulus (see page 115 of Walker-PADER, 12/16/82). Walker (PADER, 12/16/82) correctly notes that this lowering of the pH is the result of contact with the iron well casing, but he fails to recognize that such a reaction produces both hydrogen sulfide gas and an iron precipitate (Dresel and Rose, 1985) according to the following equilibrium reaction:

$$FeS_2 + 4H^+ = Fe^{2+} + 2H_2S \text{ (aq)}$$

This relationship calls into doubt the conclusion that the "black gunk" observed during the well plugging was flowing into the well bore from an open fracture (Walker-PADER, 12/16/82).

### 3.37 USGS Sampling of a Background Well, the Renkis Well (November-December 1982)

On November 24, 1982, Harry Mackey, the Erie County Oil and Gas Inspector, located a well being drilled down to the Bass Island Formation which is approximately 8 miles southwest of of the Hammermill injection wells (Walker-PADER, 12/16/82). This location is north of the Oriskany pinchout (Figure 2-2). Therefore, the Bass Island Formation would be the first porous horizon below the glacial sediments, as in the Beach No. 7 well (Walker-PADER, 12/16/82). The well's geologic similarity to and great distance from the Hammermill injection wells made it an ideal well to obtain an uncontaminated sample of the Bass Island brine. Furthermore, the owner of the well, Alan Renkis, was cooperative.

USGS was in charge of testing and sampling this well. The purposes of the work were (1) to obtain a representative fluid sample of the Bass Island Formation, and (2) to determine the hydrostatic head of the fluid at the well location (Stoner-USGS, 12/16/82). Salt water was encountered at 1,820 feet and the well produced salt water at the rate of 20-30 gpm. The Bass Island Formation fluids at this location were clear and did not have a sulfurous odor (Stoner-USGS, 12/16/82). A full suite of electric logs was run, and the temperature log indicated that the fluid level was 706 feet below surface at the time this measurement was taken (19 1/2 hours after drilling ceased) (Stoner-USGS, 12/16/82). The file copies supplied by PADER do not contain the electric logs from this well.

A sample of the Bass Island Formation from the Renkis well was used as a "background sample" to be used in comparisons with data from the Beach No. 7 well. Analytical results are more fully discussed in Section 5.0 of this report. Analytical results for inorganics from the Bass Island Formation at the Renkis well, and the seep, Bass Island, and Lockport formations at the Beach No. 7 well were all quite similar.

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There were no substantial differences that could be interpreted as indicating contamination from pulp liquor (Garnas-EPA, 2/18/83).

Organic analyses were used to attempt to obtain fingerprint of the fluids by using capillary gas chromatagraphs with electron capture detection (ECD), flame photometric detection (FPD), and thermionic specific detection (TSD). ECD and FPD provided fingerprint matches between the seep and the Bass Island Formation at Presque Isle, but there were no fingerprint matches for the samples from the Renkis well and the Lockport Formation (Garnas-EPA, 2/18/83). This evaluation corroborates the flow evidence from formation testing at Presque Isle, indicating that the Bass Island Formation was the source of the seep at that location. Concentrations of organic constituents in the fingerprint pattern recognition analyses were too low for identification by using gas chromatography/mass spectrometry (Garnas-EPA, 2/18/83).

Reference pulping liquors from the Hammermill plant were not available for comparison, because the facility had changed the chemical processes in its pulping operation in the early 1970s. The organic fingerprint patterns support the idea that the Bass Island Formation and not the Lockport Formation is the source of the seep at Beach No. 7. In addition, the background Bass Island Formation samples from the Renkis well do not match the Bass Island Formation fingerprint from the Beach No. 7 well. However, "it has not been demonstrated that the technique is measuring components from the original Hammermill pulp liquor waste" (Garnas-EPA, 2/18/83).

Two other clarifications of the data obtained from the Renkis well are quite important. First, the objective of measuring the hydrostatic head of the Bass Island Formation may not have been achieved. The field report (Stoner-USGS, 12/16/82) strongly suggests that only a single measurement of the water level was taken. Several measurements would be necessary to conclusively state that this was the hydrostatic level of the Bass Island Formation. The fluid could have still been rising at a slow rate even after 19 1/2 hours. To conclusively establish the hydrostatic level of the formation fluids, it would be necessary to *obtain several measurements over time that show the fluid was no longer rising.*

Mr. Shoener of EPA (personal communication, 3/18/87) informed Versar that only a single observation was made, because the driller would have charged $10,000 per day for down time to allow for multiple observations. The observed value does provide, at the least, minimum quantitative hydrostatic level information. Second, tannin-lignin was reported to be present in these samples, both at the "background" Renkis well and at the Beach No. 7 well. This would, on the surface, seem to indicate that tannin-lignin is a naturally occurring compound within the Bass Island Formation. Later analyses by Dr. Gillian Cooper-Driver of Boston University (EPA, 6/4/84), who used more sophisticated analytical procedures, revealed that (1) none of the samples contained simple soluble phenolics, and (2) the samples from both the Beach No. 7 and the Renkis wells contained very low levels of lignins (at the limits of detectability) that are characteristic of angiosperms and gymnosperms.

Notably, many of these compounds identified in the Renkis well were previously identified as verification compounds (Sloboda and Symms-EPA, 2/10/82). Therefore, Versar concludes that either (1) the presence of these compounds is an artifact of analytical methods, (2) the compounds occur naturally, or (3) pulping liquor is present at this location, and therefore the well is not suitable as background location. The corollaries to the third conclusion would be (1) the black fluid and associated hydrogen sulfide are not necessarily associated with the pulping liquor, and (2) the pulping liquor is disseminated over far greater areas than could be explained by the most sophisticated modeling under a preferred east-west permeability, worst-case scenario with perimeter plugging (Shoener-EPA, 10/85). This worst-case scenario was the only model that could explain both the presence of pulping liquor and pressure sufficient to cause flows to the surface through 1982.

Field blanks also contained these compounds (Cooper-Driver - Boston University/EPA, 6/4/84), and the bailer may have been contaminated with

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diesel oil (Walker-PADER, 1/7/83). Lignins were found in the Lockport and Bass Island formations, and because of the Silurian age of these formations, it is quite difficult to explain their presence.

Lignin is also highly insoluble in water. It would occur chiefly in sediment. However, 8 of the 10 samples analyzed had no sediment (Cooper-Driver-Boston University/EPA, 6/4/84). Both EPA and D'Appolonia introduced a serious procedural bias by filtering their samples for tannin-lignins. Such filtration would remove these compounds from the samples. Therefore, the analyses are not useful in determining the similarities or dissimilarities between samples and paper mill effluents (Niklas-Cornell/EPA, 5/2/83). Attempts to draw meaningful conclusions from these data area seriously undermined by the presence of these compounds (1) in rocks of these ages, (2) in the "background" Renkis well and Beach No. 7 well samples as well as in the field blanks. They are also undermined by very low concentrations of these compounds at or near detection limits and the procedural biases of the analytical techniques.

Shortly after sampling the Renkis well, USGS presented the results of their file search and literature review. This report (Click-USGS, 12/28/82) discusses the general geologic setting of the area and compares the fluids from the Beach No. 7 well with the composition of seawater and with data on oilfield brines in northwest Pennsylvania provided by Poth (1962). The report recommends that although the data were not sufficient at that time to conclusively tie the discharge at Beach No. 7 with the injection of Hammermill pulping liquor, a reasonable cause and effect relationship did exist.

3.38 FIT Domestic Well Survey (December 1982-March 1983)

Ecology and Environment presented the results of its survey of domestic wells in the Erie area in December, 1982. Eleven residential water wells were sampled on September 20 and 21, 1982, because they were near 17 gas wells that were not plugged and that penetrated the Bass

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Island Formation (Ecology and Environment-EPA, 12/6/82). These wells were sampled for 129 priority pollutants and lithium, strontium, and ammonia.

Joseph Vogel of the Erie County Health Department made several important comments on this study. Gas wells that were listed in the earlier Erie County survey (Socolow-PADER, 12/18/80) and also were the subject of the investigation (Ecology and Environment-EPA, 12/6/82) were drilled since the early to the mid-1970s. As such, it was unlikely that water would be moving up or down these wells. The casings are complete and intact, and the water-bearing zones would have been cemented off.

Mr. Vogel also noted that (1) the wells at risk would be much older than these, and (2) the older wells were largely unpermitted, and most were far too shallow to have penetrated the Bass Island Formation (Ecology and Environment-EPA, 12/6/82). Additionally, Erie County Department of Health sampled 50 residential wells within a 10-mile radius of the City of Erie (Osgood-Erie Department of Health, 1981) and analyzed the samples for chlorine, strontium, sodium, and pH. The results did not indicate a contamination problem (Ecology and Environment-EPA, 12/6/82).

The analytical results of the Ecology and Environment sampling were reported in March 1983. These results indicated that all organic priority pollutants, lithium, strontium, and ammonia reported as being present in low concentrations were of questionable validity because of sample contamination (NUS-EPA, 5/2/83). However, the levels of the organic compounds detected in this case pose no significant threat to human health (NUS-EPA, 5/2/83). Inorganic analyses indicated the presence of cadmium in the O'Hara well and of barium in the Willat well at levels that exceeded the Primary Drinking Water Standards. The analyses also indicated the presence of manganese and iron in the Gehrlein well at levels that were above Secondary Drinking Water Standards (Figure 3-9). These levels were not considered to pose risks of toxicological problems unless another source of exposure was also present (NUS-EPA, 5/2/83).

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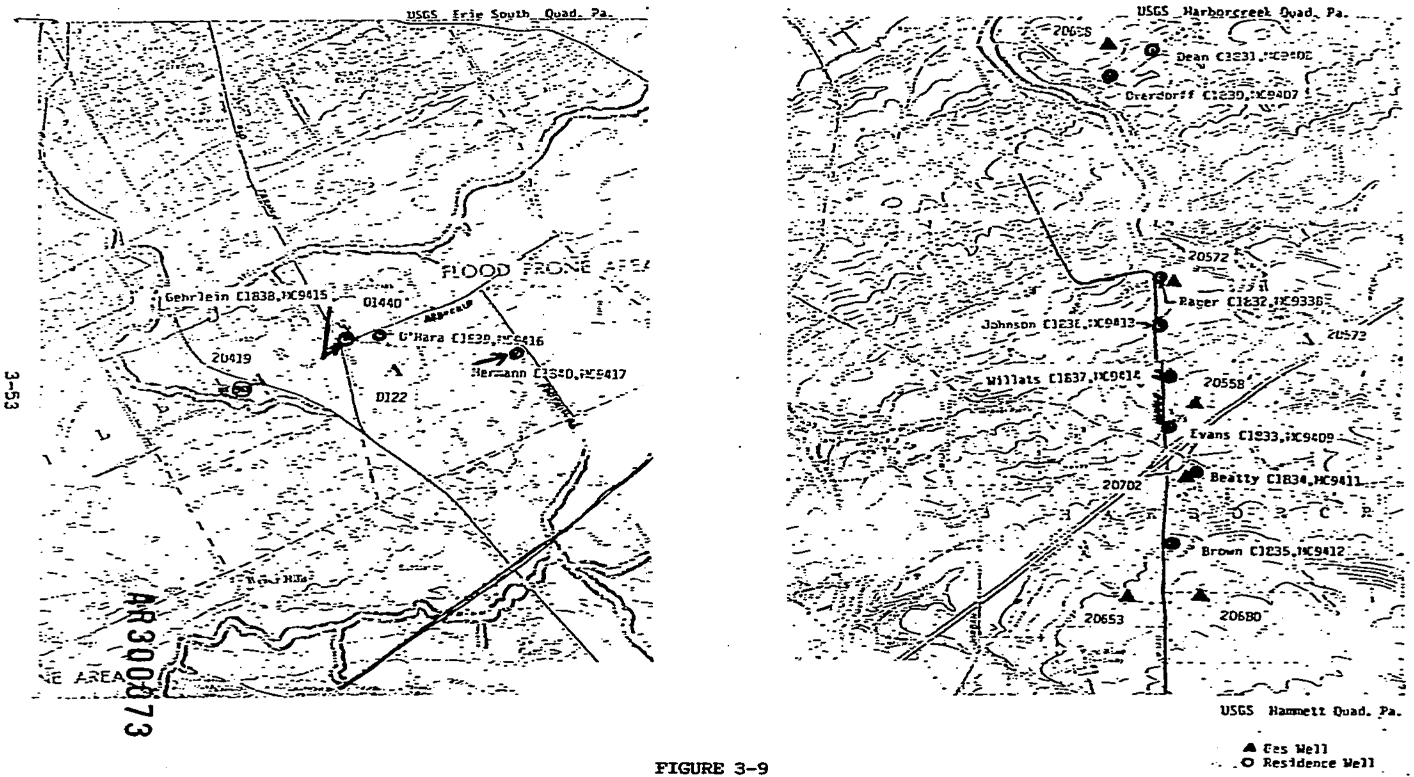


FIGURE 3-9
FIT DOMESTIC WELL SAMPLING LOCATIONS

The cover letter to the report concluded that the data were insufficient to isolate the sources of contamination for these wells, and they do not indicate a single source of contamination (Senovich-NUS/EPA, 5/2/83).

3.39 Memorial Technical High School Well (December 1982)

During the Week of December 20-24, 1982, PADER requested that the USGS assist in sampling an operating natural gas well at Memorial Technical High School (Figure 2-2). The well was being fouled by a black, odoriferous substance (Click-USGS, 12/28/82). Versar was unable to locate in EPA Region III or PADER files either the field sheets or the analytical results of the sampling. This well was drilled in 1981. During drilling, there was an unexpected show of gas containing hydrogen sulfide (650 ppm) in what was believed to be the Oriskany sandstone and which delivered an open flow of 3.5 million cubic feet per day (see well log in Memorial Technical High School file).

The Memorial Technical High School well was drilled far north of the limit of the Oriskany Formation, as shown in the literature (Figure 2-2). Geophysical logging was not used to verify the producing formation. The well log only indicates that Devonian shales are above the producing formation. John Walker indicates that this formation may be the Bois Blanc Formation that was used for the injection of Hammermill's wastes. Walker's notes on the well (contained in the Memorial Technical High School well file) indicate that he felt these fluids were "very likely Bass Island waste fluids."

Versar feels that if this hydrogen sulfide occurrence were the result of the presence of Hammermill's pulping liquor at this location, then the worst-case scenario required to explain the occurrence of chemical constituents and pressure buildup through the 1980s (Shoener-EPA, 10/85) may not be a realistic approximation of the natural conditions.

3.40 <u>NPL Published, Hammermill Comments (December 1982-March 1983)</u>

The proposed National Priorities List (NPL) was published on December 30, 1982 and the Presque Isle Beach No. 7 Well was included among the 418 sites based on the HRS Scoring model developed during the preceding summer (Ecology and Environment-EPA, 8/24/82). The listing came to Hammermill's attention in mid-January as the result of a newspaper article (Brocki-HML, 5/5/83), and Hammermill formally requested that the comment period be delayed from February 28, to April 28, 1983, to obtain and review EPA documents leading to Hammermill's inclusion on the NPL (Andrews-HML, 2/1/83).

Hammermill officials met with Mr. Shoener, the EPA Remedial On-Scene Coordinator, to discuss the inclusion of the Presque Isle site in the proposed NPL. Mr. Shoener (EPA, 2/8/83) emphasized that (1) the HRS was a technical tool, and the listing did not indict or incriminate Hammermill as having done anything wrong, illegal, or criminal, and (2) EPA felt it was reasonable and prudent to place the site on the NPL based on the reasonable cause and effect relationship suggested by high-level, competent, and responsible officials.

Following this meeting, Hammermill submitted extensive technical comments on the proposed placement of the site on the NPL. Hammermill's comments (Brown-HML, 2/24/83) included the following points:

1. There was no conclusive evidence of a connection between the Hammermill injection program and the discharge at Presque Isle.

2. The site was inappropriately scored, occasionally disregarding the instructions for completing the rating factors.

Additionally, Hammermill felt that inclusion of the site on the NPL was unwarranted, because CERCLA exempted natural gas liquids, certain activities and wastes associated with gas development, releases that result from or are involved in a state-authorized injection program, and releases that contain "de minimus" amounts of hazardous substances (Brown-HML, 2/24/83).

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Hammermill's consultants then recalculated the HRS (D'Appolonia/IT-HML, 2/24/83) to reflect its technical comments. It concluded that the site did not attain a high enough score for inclusion on the NPL (Table 3-2). Hammermill filed a suit seeking the EPA's files on the site and injunctive relief, which would have constituted an extension of the time for comment (Hammermill v. Burford-EPA, 2/25/83). Hammermill (Andrews-HML, 1/27/83 and Andrews-HML, 2/28/83) promptly made a request for documents under the Freedom of Information Act (FOIA).

Portions of Hammermill's request under the FOIA were denied, and the company appealed (Rogers and Starfield-HML, 3/23/83). Later, Hammermill began preparations to depose PADER, USGS, and EPA officials involved in the case. Later, a compromise was arranged, and the scheduled depositions were cancelled (Rogers-HML, 3/28/83).

### 3.41 First Notice of "Black Water" in Bass Island Well Logs (December 1982-January 1983)

The first indication that the Bass Island Formation might naturally contain hydrogen sulfide-bearing fluids ("black water" in driller's terminology) was a byproduct of the FIT field report. This report (Ecology and Environment-EPA, 12/6/82) contained several well logs (as attachments) that showed the occurrence of black water in wells drilled by Envirogas, Inc. John Walker also was given another log showing black water at 1,556 feet (in a limestone that could have been part of the Bass Island Formation); this occurred while drilling the Northeast Heat and Light gas well in 1914. Walker subsequently forwarded that log to Mr. Shoener (Walker-PADER, 1/25/83). However, Mr. Kevin Carrol of Envirogas, Inc. indicated that the Bass Island brine was characterized as a clear, high-chloride brine that was not sulfurous (Walker-PADER, 1/25/83).

### 3.42 D'Appolonia Interim Report (March 1983)

Further information on the possible natural occurrence of black water within the Bass Island Formation was supplied in the "Presque Isle State Park Gas Well Investigation, Interim Report (D'Appolonia/IT-HML,

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3/83)." D'Appolonia presented well logs from 17 Erie County gas wells drilled in 1914, 1960, and 1977-1979 where the occurrence of black water in the Bass Island horizon was noted and four wells drilled in 1932-1942 where flowing artesian conditions were noted (Figure 3-10). D'Appolonia argued that both the pressure drive and chemical makeup of the seep at Presque Isle could be the result of natural conditions (D'Appolonia/IT-HML, 3/83).

The report compared chemical evidence gathered at the Beach No. 7 well. In the report, it was suggested that all of the compounds detected could reasonably be explained by naturally occurring brine and petroleum geochemistry, and examples from the literature were offered to support these concepts (D'Appolonia/IT-HML, 3/83). D'Appolonia learned through personal communication with Van Tyne Consultants that black water occurrences in the Bass Island Formation were reported by the oil and gas industry in some regions.

The Bass Island artesian conditions had been mentioned in the original injection well feasibility study (Dow-HML, 11/19/62) in its discussion of well fill-up as an indicator of formation porosity and permeability. D'Appolonia (HML, 3/83) proposed an explanation of the artesian conditions based on the elevation of the recharge areas in Canada (Figure 3-11) as a classic confined aquifer model. Versar feels that lithostatic pressure is probably a more important factor in determining natural artesian conditions at these depths. However, in the absence of any meaningful hydrostatic level data, nothing conclusive can be said regarding the correctness of this approach.

Tritium and carbon-14 dating of the samples obtained from the Bass Island Formation were attempted. However, the results were inconclusive. Tritium samples were exposed to the atmosphere and drilling fluids during drilling and sampling. Carbon-14 analyses gave dates that were far too young or far too old to be attributed to the pulping liquor (D'Appolonia/IT-HML, 3/83).

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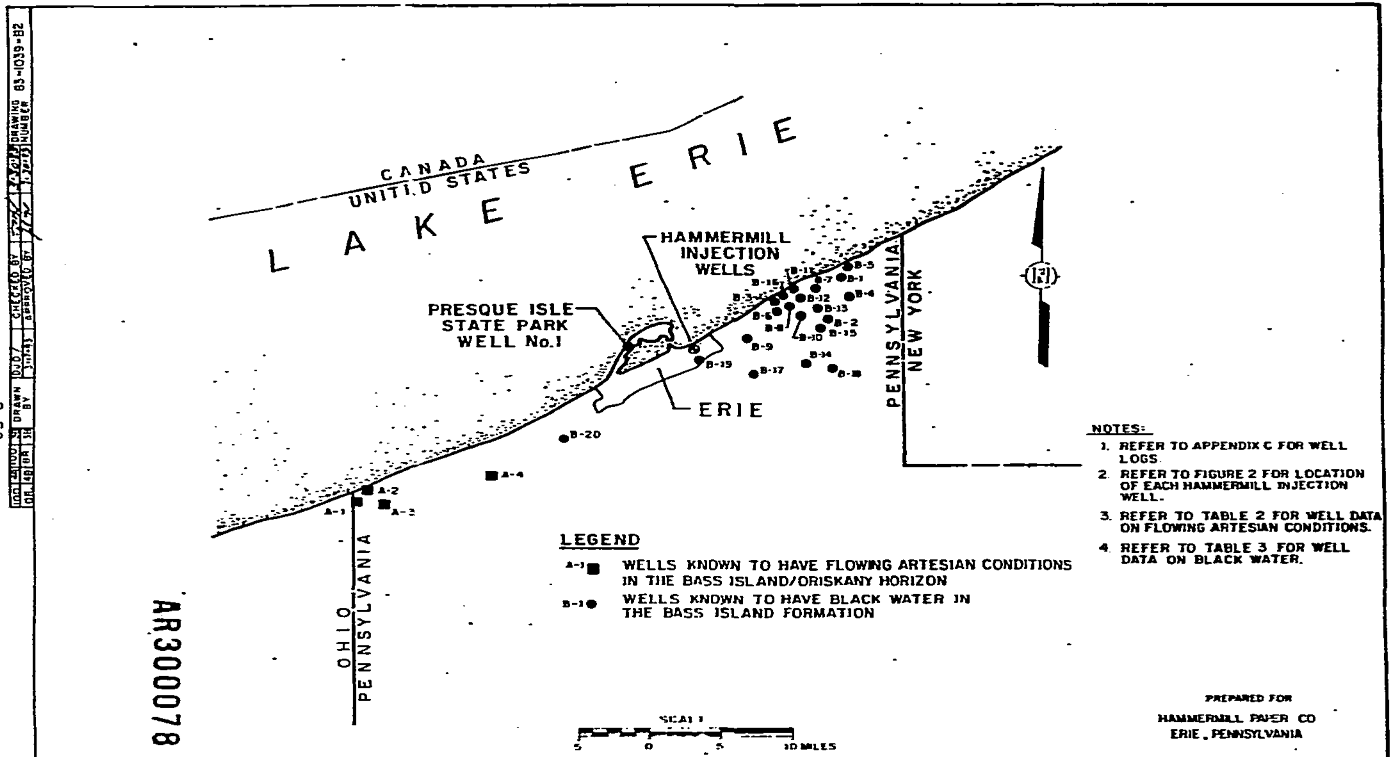


FIGURE 3-10
LOCATION OF WELLS WITH BLACK WATER OR
FLOWING ARTESIAN CONDITIONS IN ERIE, PENNSYLVANIA, AREA

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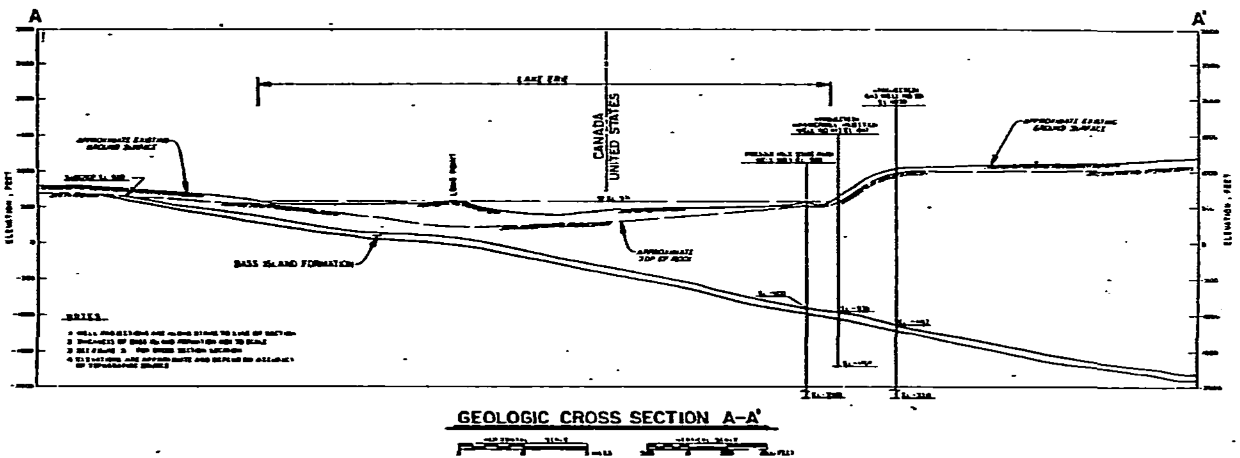


GEOLOGIC CROSS SECT.ON A-A'

PREPARED FOR

HAMMERMILL PAPER CO
ERIE, PENNSYLVANIA

D'APPOLONIA

DRAWING NUMBER 83-1039-E3

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FIGURE 3-11
CROSS SECTION INDICATING D'APPOLONIA (HML, 3/83) EXPLANATION
FOR ARTESIAN CONDITIONS OF THE BASS ISLAND FORMATION

Modeling presented in this report (D'Appolonia/IT-HML, 3/83) was performed by using a finite element model to separately evaluate the pressure buildup and mass transport of the injection program under two permeability scenarios: First, by assuming a permeability of 230 millidarcies for the Bass Island Formation, and second, by using a value of 2,300 millidarcies. This model is discussed at length in Section 6.0 of this report. The model assumed a homogeneous reservoir for waste injection based on a lineament study that suggested that there was no dominant fracture trend in the area (Figure 3-12). The central findings of modeling are as follows: If the permeability of the formation was high enough to allow the concentration gradient of the pulping liquor to reach the Beach No. 7 well, then the pressure buildup was insufficient to cause flow. Conversely, if the permeability of the formation was low enough to induce flow, then the contaminants would never have reached the Beach No. 7 well (D'Appolonia/IT-HML, 3/83).

Versar asked Hammermill and IT (formerly D'Appolonia) representatives whether the model would be interpreted correctly by stating that it was possible that either a natural artesian drive could have forced the contaminants out of the Beach No. 7 well, or that the Hammermill pressure drive could have forced a naturally occurring fluid from the formation, but not both. They agreed that this was a correct interpretation (A. Brosig-HML and J. Wright-IT, personal communication, 12/10/86). Therefore, if the Bass Island Formation were under sufficient natural artesian pressure to flow or nearly flow, then this modeling would clearly indicate the possibility of Hammermill's inducement of the flow of a naturally occurring fluid.

3.43 <u>EPA Obtains Academic Consultants (April-June 1983)</u>

Following the submittal of the D'Appolonia report (HML, 3/83), EPA obtained several consultants from major universities to review the report and to examine specific technical aspects of the investigation. EPA contracted the services of specialists in paleobotany and petroleum reservoir simulation.

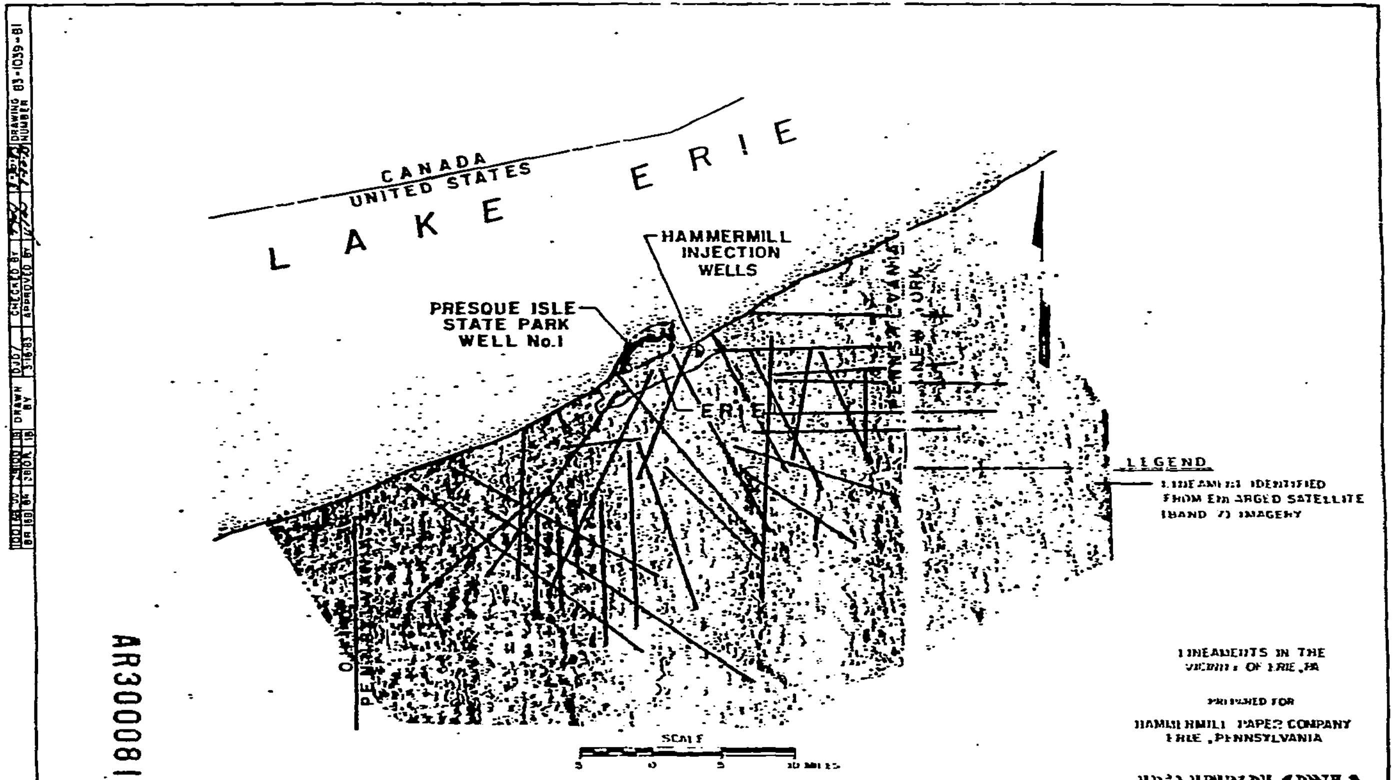


FIGURE 3-12
MAP OF LINEAMENTS IN THE VICINITY OF ERIE, PENNSYLVANIA, PREPARED BY USING LANDSAT (BAND 7) IMAGERY

Dr. Leonard Koederitz of the University of Missouri-Rolla (UMR) performed pressure contour modeling of the Hammermill injection program and its effect on the Beach No. 7 well. In his initial findings, Dr. Koederitz (UMR/EPA, 4/21/83) determined that the calculations performed by Kleeman (EPA, 4/30/82) were unreliable, because they had employed unrealistically high values for the injection pressure. Preliminary modeling indicated that the Beach No. 7 well would have experienced a rise in pressure of 77 psi by January 1, 1972, but the pressure would have declined by 61 psi to only 16 psi by January 1, 1983.

Dr. Koederitz later submitted further modeling results, presenting 19 different scenarios corresponding to varying reservoir parameters, including permeability and thickness. Additionally, these parameters were modeled to observe the pressure buildup and decline at the Beach No. 7 well at three different times: (1) November 1970, when two of the three wells were still injecting (maximum), (2) January 1972, to model pressure decline following the cessation of injection, and (3) January 1983, to model the current situation (Koederitz-UMR/EPA, 5/23/83). Dr. Koederitz determined that if the reservoir parameters were as modeled by D'Appolonia (HML, 3/83), then the well would not have flowed to the surface. However, if the reservoir were as described by D'Appolonia (HML, 7/19/79), the well would have flowed to the surface (Koederitz-UMR/EPA, 5/23/83).

None of the 19 modeling scenarios proposed in the Koederitz studies had been able to explain how sufficient pressure could be maintained at the Beach No. 7 well through 1983 because of the rapid pressure dissipation after the cessation of injection (Koederitz-UMR/EPA, 5/23/83). Dr. Koederitz noted that although the preliminary fracture trace and lineament map had shown the possibility of extensive fractures near the Beach No. 7 well and the Hammermill facility, later studies suggested only moderate fracturing in the Erie area and no fracturing in the vicinity of the Beach No. 7 well or the Hammermill well (Koederitz-

UMR/EPA, 5/23/83). The lineament analyses issue will be discussed in Section 4.0 of this report.

Dr. Koederitz thought that plugging of the pore spaces due to reactions between the formation and the injected liquor might explain the continued pressure drive through the early 1980s (Koederitz-UMR/EPA, 6/30/85). The permeability/plugging effect could be proven by obtaining a core analysis of the Bass Island Formation, but because there were no original (uninjected) cores available for comparison, this might prove to be inconclusive (Koederitz-UMR/EPA, 6/30/85).

To assess the organic geochemical aspects of the D'Appolonia (HML, 3/83) report, EPA contacted Dr. Karl Niklas of Cornell University. Dr. Niklas is an expert on the occurrence of lignin in Silurian age rocks and fossils (see Niklas and Pratt, 1980). Niklas concluded that the tannin-lignin discussions were inconclusive, because (1) linins would have been bound to protein-rich bacteria and cellulose during filtering and would have been removed, and (2) the samples would have had to been oxidized with nitrobenzene to observe some of the important verification compounds (Niklas-Cornell/EPA, 5/2/83). Dr. Niklas (Cornell/EPA, 5/2/83) felt that D'Appolonia's (HML, 3/83) contention that much of the seepage at the Beach No. 7 well could be explained by a natural petroleum origin was not unreasonable, but this was not proven; the organic profiles of fossil fuels are very similar in many respects with the profiles of organic debris recently derived from living plants and animals.

Dr. Niklas (Cornell/EPA, 6/8/83a) reviewed several PADER reports, and he felt that the presence and concentrations of abietic and dehydroabietic acids, diethyl phthalates, fluoranthrene/pyrene, and resin acids clearly implicate human agents. He made these assertions, because these compounds are common paper additives (plasticizers and coatings) used in the paper industry (Niklas-Cornell/EPA, 6/8/83a). However, Dr. Niklas was probably not aware that it was unlikely that paper additives were ever in the injection liquor (Brown and Spalding, 12/66).

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Dr. Niklas is experienced in Carboniferous coals. He states that anthracenes/phenanthrenes had been reported in coal but only if the coal had been treated vigorously with oxidizing agents (Niklas-Cornell/EPA, 6/8/83a). He does not mention natural gas or petroleum sources for these compounds, but believes that the strata present at the Beach No. 7 well are too old to have yielded the observed concentrations of compounds (Niklas-Cornell/EPA, 6/8/83a). Dr. Niklas (Cornell/EPA, 6/8/83b) recommended that Dr. Gillian Cooper-Driver of Boston University, one of the world's authorities on phenolics (tannins, etc.), be retained to assist in the investigation.

### 3.44 EPA Seeks Monitoring Well to Obtain Injected Pulping Liquor (May-October 1983)

The lack of an actual sample of the pulping liquor injected into the Bass Island Formation and desire for information on the formation porosity and permeability caused EPA to consider drilling a 1,600-foot deep well near the Hammermill injection wells. EPA requested that Hammermill pay for the installation of this well (Wasserburg-EPA, 5/3/83).

Hammermill responded that the company had already expended considerable funds and that it was reluctant to spend $150,000 to drill a monitoring well and to test the fluid in this horizon (Rogers and Starfield-HML, 8/3/83). Hammermill suggested instead that EPA undertake sampling at two proposed gas wells: the Wayne Street well located 1.5 miles from Hammermill, and the Vincent High School well, located 3.5 miles away (Figure 2-2). Hammermill declined to participate in such sampling, because the cost was anticipated to be between $30,000 and $45,000, not including analytical costs (Rogers and Starfield, 8/3/83).

Hammermill later decided that it would neither construct a deep monitoring well itself nor provide funds for another party to do so (Rogers-HML, 10/20/83). Hammermill came to this decision "because EPA was not able to assure them that there existed any combination of

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conditions in the Bass Island horizon that would would put an end to the need for further well-drilling, that EPA would determine that a number of wells would be needed to answer diverse theoretical questions that would make the present effort merely the first step in a complex and expensive testing campaign" (Rogers-HML, 10/20/83). Hammermill offered to discuss granting federal and state officials access to its property to allow the drilling of a well at government expense (Rogers-HML, 10/20/83). EPA's contractor, NUS Corporation, requested estimates and learned that the costs to drill to the core point would be $70,000-$80,000 plus an additional $100,000 to obtain a core (Angerman-EPA, 10/26/83).

3.45 Envirogas, Van Tyne Consultants Inquiries, UIC Critique (May-July 1983)

After the D'Appolonia report was released, EPA contacted Mr. Kevin Carrol, Vice President of Geology and Exploration for Envirogas, Inc., to discuss the 17 references to "black water" in the Envirogas drillers' logs (Shoener-EPA, 5/18/83). Mr. Carrol responded that the drillers were inexperienced and that one should not depend on the well logs as being an accurate characterization of the Akron (Bass Island equivalent) brines. However, he also stated that in some cases, this could be possible (Carrol-Envirogas, 5/25/83).

Van Tyne Consultants were cited as a reference for naturally occurring black water brines in the D'Appolonia (HML, 3/83) report. Mr. Shoener contacted Arthur Van Tyne who told him that in western New York, the Bass Island Formation is much thinner, and where the formation is extensively fractured, it occasionally produces a black water brine, but the occurrences are not regional (Walker-EPA, 7/7/33).

Versar contacted Mr. Van Tyne, and he reiterated that the occurrence of black water is highly variable. One well may produce black water, but 500 yards away, it may produce a clear brine (Van Tyne, personal communication, 2/10/87). Mr. Van Tyne indicated that the occurrence of black water was a localized phenomena and that Carrol would have been correct in characterizing the Bass Island brine as clear, but the Envirogas drillers may not have been mistaken, because such occurrences are not unusual in the fractured Bass Island reservoirs of the adjacent county in New York (personal communication, 2/10/87).

EPA asked the Underground Injection Control (UIC) unit at EPA Region III to examine the Hammermill injection system under the forthcoming UIC regulations. One criticism voiced by the UIC unit (Kleeman-EPA, 5/26/83) was that the radius of the endangering influence to ground water was not properly defined through pressure decline calculations. However, the feasibility study did mention potential problems from gas wells located near the injection wells (Dow-HML, 11/19/62). The study also contained calculations, however flawed, concerning the radius of influence. Acceptable pressure decline models were not available in 1962.

Another serious deficiency noted in the permits was the lack of an injection pressure limitation (Kleeman-EPA, 5/26/83). UIC regulations for this system would have placed a ceiling of 472 psi on the surface pressure (Kleeman-EPA, 5/26/83). A formation will usually fracture when injection pressures exceed 0.5-1.5 psi per foot of depth at the formation face (McLean, 1968). Adding 718 psi for the pressure exerted on the formation by the column of water in the well casing to the 1,250 psi leads to 1,968 psi of pressure exerted on the formation face at the Hammermill wells. This figure is well above McLean's (1968) lower bound of 810 psi, but it is well below the upper bound (2,430 psi) for this well.

Actual data on the susceptibility of the Bass Island to pressure-induced fracturing is available:

1. Hammermill 1 would not take fluid even at 2,500 psi (surficial pump pressure) before acidization, and the formation break occurred at 1,400 and 3,000 psi.

2. Hydrofracture of Hammermill 2 required 1,850 psi (Waldron-HML, 6/13/72).

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Therefore, although the pressures under which Hammermill operated were excessive, there is no conclusive indication that hydrofracturing occurred as a result of normal operating pressures.

Another UIC criticism was that no tests were made to determine the compatibility of the injection fluid with the casing fluids, and no routine inspections were made (Kleeman-EPA, 5/26/83). This point is quite valid, and such practices might have prevented the blowout of Hammermill 1 during 1968. Additionally, continuous monitoring of the injection pressures or of the surrounding ground water was not apparent (Kleeman-EPA, 5/26/83).

### 3.46 Hammermill Submits Final Comments on Inclusion on NPL (June 1983)

In June 1983, Hammermill submitted its final set of comments on the proposed inclusion of the site in the NPL (Rogers-HML, 6/27/83). These comments were incorporated in Hammermill's technical review of documents released under the FOIA (D'Appolonia/IT-HML, 3/83; 5/25/83; 6/8/83; 6/20/83; and 6/24/83).

### 3.47 PADER Rebuttal to D'Appolonia's March 1983 Report

In July 1983, John Walker responded to the D'Appolonia (HML, 3/83) report during a point-by-point discussion with an intern for the PADER attorneys (McGregor-PADER, 7/14/83). Walker later prepared a more complete report (Walker-PADER, 8/15/83) that reflected these criticisms, included a geologic description of the area, and incorporated his theory as described in the preceding sections of this summary. Walker's key criticisms were as follows:

1. The difference in elevation suggested by the artesian flow argument could only account for a 36-psi pressure differential on the recharge area, and this was insufficient to overcome friction, porosity, and permeability variations over the 70 miles between the recharge area and Presque Isle.

2. Outcrops of the Bass Island Formation below Lake Erie would have negated much of this effect at any rate.

3. The Beach No. 7 well would be influenced more by the 1,200-psi injection pressure 4.5 miles away than it would by 36 psi of head 70 miles away (McGregor-PADER, 7/14/83).

Versar wishes to note that the original shut-in pressure on the Beach No. 7 well was approximately 34-36 psi when the well first stabilized. As stated before, the artesian flow argument of D'Appolonia cannot be definitively supported or refuted without additional hydrostatic information. Additionally, Walker later discovered that the Bass Island brine flowed to the surface in the Norfolk District of Ontario, and the formation fluid, even though clear, had a sulfurous odor (Trevail, 8/5/83).

Walker further commented that although there are artesian conditions in the Oriskany Formation (same approximate stratigraphic position as Bass Island Formation (D'Appolonia/IT-HML, 3/83)), this argument was not applicable to the Bass Island Formation, and the Bass Island does not flow to the surface in Pennsylvania (McGregor-PADER, 7/14/83). Walker noted that the Bass Island fluid level was 862 feet in the Hammermill 1 well when it was observed during drilling.

D'Appolonia (HML, 3/83) reasoned that based on the number of lineaments and their variable orientations, secondary permeability on a regional basis would be fairly uniform in all directions. Walker (McGregor-PADER, 7/14/83) had the following responses:

1. This was simply the old concentric flow pattern that had been discredited by PADER.

2. Flow from the injection wells would move along directional high-permeability zones in an anisotropic pattern.

3. The distance between lineaments averages 2 miles; therefore, the D'Appolonia lineament analysis suggests that the flow pattern is "undoubtedly anisotropic due to fractures."

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The concentric flow pattern invalidates the D'Appolonia mass transport analysis (McGregor-PADER, 7/14/83). Both D'Appolonia and Walker make classic errors in their interpretation of lineaments; these errors will be discussed in Section 4.0 of this report.

Walker was critical of D'Appolonia's (HML, 3/83) contention that the occurrence of black water in the Lockport Formation was well known. Walker noted (McGregor-PADER, 7/14/83) that the Lockport Formation brine contained 1 ppm hydrogen sulfide, while the Bass Island brine had concentrations as high as 23,000 ppm. Versar feels it is very important to note that the 23,000 ppm figure is not a measure of the amount of hydrogen sulfide in the formation fluid, but it was obtained during the sampling of the gas cap that accumulated before the well was vented.

D'Appolonia (HML, 3/83) noted the occurrence of black water in the Bass Island Formation that Walker attributed to inexperienced drillers. Walker also noted that any wells drilled after 1977 probably encountered Hammermill waste in the Bass Island Formation (McGregor-PADER, 7/14/83). Furthermore, neither the drillers at the Beach No. 7 well nor the Hammermill 1 well noted black water when these wells were drilled (McGregor-PADER, 7/14/83). If the well records are not in error and these post-1977 wells do show evidence of pulping liquor, as Walker suggests, then the Hammermill pulping liquor has migrated over a much larger area than would be allowed by the worst-case scenario (Shoener-EPA, 10/85), and the pressure drive needed to cause a flow at the Beach No. 7 well through the early 1980s could not be explained by the Hammermill injection program.

D'Appolonia (HML, 3/83) stated that both the Bass Island and Lockport formations produced flowing artesian conditions. Walker objected, stating that the Bass Island Formation flowed to the surface overnight, but the Lockport Formation did not (McGregor-PADER, 7/14/83). The fact that the Lockport fluid did not fill up the well overnight is not an indication that the formation does not have a flowing artesion condition, only that the Lockport Formation porosity and permeability are low; when the Lockport Formation was properly packered off, the drilling fluids were flowing from the well head (Walker-PADER, 12/6/82 and Wright-HML, 11/16/82). This does not necessarily mean that the Lockport fluid would have flowed to the surface (because of the lower specific gravity of the water that circulated in the hole). The fact that the well did not fill up overnight is not relevant to the question of hydrostatic potential.

D'Appolonia (HML, 3/83) noted that natural gas was detected in the Bass Island Formation during the plugging and testing program. Walker (McGregor-PADER, 7/14/83) replied that a very slight bubbling of gas was observed, and that natural gas was practically nonexistent, if present at all. After a review of the testing and plugging records (Walker-PADER, 11/16/82 and Wright-HML, 12/16/82), Versar is unsure of the basis of Walker's contention that natural gas may not have been present at all. The bubbling gas was observed and ignited after the Lockport Formation was cemented off, and a packer was emplaced to isolate the formation.

D'Appolonia (HML, 3/83) also stated that the well contained extraneous material, such as wood, leaves, a material similar to plumbers' oakum (a fibrous material, such as hemp, impregnated with oil), metal trash, bridge plugs, and packer seats probably made of lead (from cuttings washed to the surface). D'Appolonia (HML, 3/83) considered chemical interaction between the well casing, the extraneous material, and the brines to be likely. Walker replied that this was totally wrong and misleading (McGregor-PADER, 7/14/83).

Upon closer examination of the plugging and testing record (Walker-PADER, 12/16/82), Versar finds that this extraneous material was located within the 3-inch tubing, and therefore, it would have been isolated from the Bass Island fluids. However, the recent work of Dresel and Rose (1985) indicates that sulfurous brines interact strongly with metal casing materials, possibly producing sampling artifacts.

D'Appolonia (HML, 3/83) stated that the original well log did not indicate the occurrence of black water in either the Lockport or the Bass Island formation; however, the well log did show that the Bass Island Formation produced water and had to be cased through this level, suggesting that the formation produced a substantial amount of fluid when it was drilled. Walker responded that "obviously the Bass Island did not flow to the surface; if it had, it would have been recorded on the detailed well record (McGregor-PADER, 7/14/83." This statement is a supposition, not a technical comment.

D'Appolonia (HML, 3/83) also mentions that the concentrations of both sulfide and sulfate are significantly higher in the Lockport Formation than in the Bass Island Formation. Walker responds that since the Lockport Formation may have been pressurized by Hammermill's injection program, the formation may now be contaminated by Bass Island fluids through old unplugged wells (McGregor-PADER, 7/14/83). Again, accepting such a conclusion might invalidate the worst-case scenario (Shoener-EPA, 10/85) required to maintain flow at the Beach No. 7 well into the early 1980s, because the reservoir would be greater than 20 feet thick if the Lockport Formation were linked, as Walker suggests.

Walker criticizes D'Appolonia for maintaining that boron, ammonia, and titanium were not present above trace levels in the injection liquor, and for stating that their occurrences are probably natural; D'Appolonia cites brine analyses from New Mexico as an example (D'Appolonia/IT-HML, 3/83). Walker states that USGS brine analyses (Poth, 1962) show the concentrations of these substances are not natural. Walker also states that according to Brown and Spalding (HML, 12/66), titanium dioxide was present in the injection liquor (McGregor-PADER, 7/14/83 and Walker-PADER, 8/15/83). Here again, Walker quotes Brown and Spalding (HML, 12/66) completely out of context, even after Hammermill supplied to PADER a copy of the article with the pertinent passages underlined (see Brown-HML, 3/26/81).

The figures in D'Appolonia (HML, 3/83) provided the following additional comments from Walker (McGregor-PADER, 7/14/83):

1. The lineament analysis indicates that an east-west fracture lineament passes through both the Hammermill injection system and the Beach No. 7 well.

2. The wells drilled in 1914 and 1960 occurred in an old gas field and were drilled to the Medina Formation (see Figure 1-2).

Therefore, abandoned unplugged gas wells could have provided an avenue for the entrance of Lockport brines to the Bass Island Formation near these wells. However, Walker (PADER, 8/15/83) does not indicate the abandoned gas wells to which he is referring.

Walker included these comments, a site history, and his previously outlined theories in a technical report (Walker-PADER, 8/15/83). In the report, he concluded that the connection between the Hammermill injection program and the discharge of hydrogen sulfide-bearing fluids was supported by (1) the timing of fluid flow at Presque Isle, (2) geology and fracturing, (3) the pressure of injection and the potential for hydrofracturing of the Bass Island Formation, and (4) a comparison of the composition of the injected waste to the composition of the discharge. Walker (PADER, 8/15/83) closed by accusing Hammermill of permit violations, and he noted the implications of this case for siting future underground injection well systems.

### 3.48 Erie School Board Gas Well Investigations (August-September 1983)

Hammermill's consultant, D'Appolonia, transmitted a proposed testing and sampling plan for the gas wells that Hammermill suggested for study in lieu of drilling a deep monitoring well (Wright-HML, 8/22/83). These were the Wayne Street and Vincent High School wells (see Figure 2-2 for locations). EPA learned that the contractor would charge $10,000 a day for down time while coring and testing the Bass Island Formation (Walker-PADER, 8/24/83), and that Hammermill had decided not to fund the investigation (Walker-PADER, 8/29/83). EPA also concluded that the costs

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involved in coring and sampling these wells were too great (Walker-PADER, 9/7/83).

Samples from the Wayne Street well were obtained by the USGS and were sent to EPA's Denver laboratory for analysis (Walker-PADER, 9/16/83). Unfortunately, soap was used in the drilling fluid, and this severely limited the usefulness of the analyses (Shoener-EPA, 10/85).

The Bass Island Formation fluid at the Vincent High school well (Figure 2-2) contained no black water, and it flowed only at a trickle (Walker-PADER, 9/12/83a). Hammermill's Mr. Brosig informed Mr. Shoener that the drillers had penetrated the Bass Island Formation and shut down operations to observe Bass Island fluid flows into the hole. John Walker interpreted this as indicating that the formation was relatively unfractured at this location, and it therefore contained only the clear, native salt water in the intergranular pores of the reservoir (Walker-PADER, 9/12/83a).

The fluid from the Bass Island Formation at the Wayne Street well (Figure 2-2) was also a clear brine (Walker-PADER, 9/16/83a). No hydrogen sulfide odor was detected. However, an odor of methane was detected above the Bass Island Formation. Conductivity readings for the drilling fluids increased sharply when the Bass Island Formation was penetrated (Walker-PADER, 9/16/83). This suggests that the formation had a good flow of fluids into the borehole, and therefore, the formation has good porosity and permeability in this location.

### 3.49 Hammermill Submits Information on Neutracel (September-October 1983)

Hammermill internal correspondence (Brown-HML, 9/20/83) regarding the acids used in their neutral-sulfite pulping process (Neutracel) was contained in PADER correspondence files. Presumably this information was submitted in response to Wasserburg's (EPA, 5/3/83) letter indicating that a monitoring well was needed because, samples (or other detailed information) of the pulping liquor were not available. Analysis of a concentrated sample (taken from Dr. Brown's notebook, dated 1/15/51) indicated that the volatile acids consisted largely of acetic acid.

EPA contacted Hammermill's legal representatives and requested further information. Specifically, EPA was interested in how the pulping liquor that was washed with city water (and later injected) compared with the concentrated sample analyzed by Dr. Brown in 1951 (Gray-EPA, 10/12/83).

### 3.50 Final EPA Response to Hammermill Comments on Inclusion in the NPL (September 1983)

The final NPL was published during September 1983, and it included the Presque Isle site. EPA responded to a number of comments submitted by Hammermill during the spring and summer of 1983. Hammermill had voiced three principal objections:

1. Insufficient time was allotted to obtain and review pertinent EPA files to respond to EPA's allegations.
2. EPA's procedure made no provisions for interested parties to submit comments and to use the HRS to delete sites.
3. The HRS was inappropriately applied to the Presque Isle site (EPA, 9/83).

In response to the first comment, EPA (9/83) noted that essentially all information used to score the site was included in the public docket, and although the deadline for comments was not formally extended, EPA had accepted and considered all Hammermill submittals through July 1983. To Hammermill's second comment that the procedure to delete sites was too restrictive, EPA (9/83) replied with an admonition that the published procedures are guidance and that the agency does not expect to delete sites based on revisions to the HRS score for a variety of reasons. Actual decisions about what factors will be used to delist sites would be made on a case-by-case basis as individual sites are considered for deletion, taking into account the guidance criteria and any other appropriate factors (EPA, 9/83).

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EPA (9/83) responded on a point by point basis to Hammermill's third assertion that the HRS was inappropriately applied to the Presque Isle site (Table 3-2). First, according to EPA (9/83), there was sufficient evidence to link Hammermill's injection program to the seepage that took place at the Beach No. 7 well, because both the seep and injection zone involved the Bass Island Formation. Furthermore, there was sufficient cause to be concerned that other abandoned wells of similar age and construction in the area also posed a threat to the shallow aquifer used as a source of drinking water (EPA, 9/83). Secondly, EPA determined the most likely source of the fluid was the Hammermill pulping liquor based on the presence of resin acids, phthalates, hydrogen sulfide, and other compounds that may be reasonably linked to the pulping process (EPA, 9/83). However, the assumption that Hammermill's waste was the source of the discharge was relied upon only in determining the quantity of waste factor. Furthermore, placing the Presque Isle site on the NPL does not constitute any determination of responsibility or liability (EPA, 9/83).

Analytical results for the fluids from the Beach No. 7 well versus the background of the Bass Island aquifer indicate that a reasonable basis exists for the conclusion that the injection of pulping wastes bears a causal relationship to the fluids in the Bass Island Formation (EPA, 9/83). EPA (9/83) felt that the citation of information in technical reports on the characteristics of oil- and gas-bearing strata in California was inappropriate, because exploratory borings in the Erie area indicate that the Bass Island Formation naturally contains a clear, high-chloride brine. The timing of fluid flow at Beach No. 7, the pre-injection pressure data, and information from the Renkis well indicate that the Bass Island Formation pressure is not normally sufficient to cause fluid flows to the surface (EPA, 9/83).

EPA (9/83) agreed that if the aquifer of concern is the surface aquifer, then there was no basis to score an observed release, because contamination of the surface aquifer had not been measured. EPA therefore revised its scoring on this parameter from 45 to 0.

TABLE 3-2
HAMMERMILL'S COMPARISON OF EPA AND D'APPOLONIA
HRS MODEL SCORES FOR THE PRESQUE ISLE SITE
(Table 1 from D'Appolonia-HML, 2/24/83)

| RATING FACTOR | ORIGINAL EPA SCORE | | WELL IS THE FACILITY: D'APPOLONIA PROPOSED SCORE | | WELL IS THE FACILITY: REASON FOR SCORE VARIANCE | BASS ISLAND Fm. IS THE FACILITY; WELL IS POTENTIAL DISCHARGE POINT: D'APPOLONIA PROPOSED SCORE | | BASS ISLAND Fm. IS THE FACILITY; WELL IS POTENTIAL DISCHARGE POINT: REASON FOR SCORE VARIANCE |
|---|---|---|---|---|---|---|---|---|
| **MIGRATION** | | | | | | | | |
| GROUND WATER ROUTE | | | | | | | | |
| (1) Observed Release | | 45 | | =(0) | a | | =(0) | e |
| (2) Route Characteristics | | | | | | | | |
| Depth to Aquifer of Concern | | | 6 | | | 6 | | |
| Net Precipitation | | | 0-3 | | | N/A | | |
| Permeability Unsaturated Zone | | | 3 | | | N/A | | |
| Physical State | | | 3 | | | 3 | | |
| Total | | =(N/A) | | 15 | N/A | | 9 | N/A |
| (3) Containment | | =(N/A) | | 1 | b | | 1 | b |
| (4) Waste Characteristics | | | | | | | | |
| Toxicity/Persistence | 18 | | 0 | | c | 0 | | c |
| Hazardous Waste Quantity | 8 | | 0 | | d | 0 | | d |
| Total | | 26 | | 0 | N/A | | 0 | N/A |
| (5) Targets | | | | | | | | |
| Ground Water Use | 9 | | 9 | | | 0 | | |
| Distance to Nearest Well/ Population Served | 5 | | 5 | | | 0 | | |
| Total | | 14 | | 14 | N/A | | 0 | e |
| Total Ground Water Route Score [(1)x(2)x(3)x(4)x(5)/57,330]x100 = $S_{gw}$ | | 28.57 | | 0 | | | 0 | |
| SURFACE WATER ROUTE | | | | | | | | |
| (1) Observed Release | | =(0) | | =(0) | N/A | | =(0) | N/A |
| (2) Route Characteristics | | | | | | | | |
| Facility Slope and Intervening Terrain | 0 | | 0 | | | 0 | | |
| 1-Year, 24-Hour Rainfall | 2 | | 0-2 | | | 0-2 | | |
| Distance to Nearest Surface Water | 6 | | 6 | | | 6 | | |
| Physical State | 3 | | 3 | | | 3 | | |
| Total | | 11 | | 11 | N/A | | 11 | N/A |
| (3) Containment | | 3 | | 1 | b | | 1 | b |
| (4) Waste Characteristics | | | | | | | | |
| Toxicity/Persistence | 18 | | 0 | c | | 0 | | c |
| Hazardous Waste Quantity | 8 | | 0 | d | | 0 | | d |
| Total | | 26 | | 0 | N/A | | 0 | N/A |
| (5) Targets | | | | | | | | |
| Surface Water Use | 6 | | 6 | | | 6 | | |
| Distance to a Sensitive Environment | 2 | | 2 | | | 2 | | |
| Population Served/Distance to Water Intake Downstream | 0 | | 0 | | | 0 | | |
| Total | | 8 | | 8 | N/A | | 8 | N/A |
| Total Surface Water Route Score [(1)x(2)x(3)x(4)x(5)/64,350]x100 = $S_{sw}$ | | 10.67 | | 0 | | | 0 | |
| AIR ROUTE | | | | | | | | |
| (1) Observed Release | | 45 | | 0 | f | | 0 | f |
| (2) Waste Characteristics | | | | | | | | |
| Reactivity and Incompatibility | 0 | | 0 | | | 0 | | |
| Toxicity | 9 | | 0-9 | | | 0-9 | | |
| Hazardous Waste Quantity | 8 | | 0-8 | | | 0-8 | | |
| Total | | 17 | | 17 | N/A | | 17 | N/A |
| (3) Targets | | | | | | | | |
| Population Within 4-Mile Radius | 21 | | 21 | | | 21 | | |
| Distance to a Sensitive Environment | 2 | | 2 | | | 2 | | |
| Land Use | 3 | | 3 | | | 3 | | |
| Total | | 26 | | 26 | N/A | | 26 | N/A |
| Total Air Route Score [(1)x(2)x(3)/35,100]x100 = $S_a$ | | 56.67 | | 0 | | | 0 | |
| **MIGRATION HAZARD MODE SCORE** $\sqrt{S_{gw}^2 + S_{sw}^2 + S_a^2}/1.73 = S_M$ | | 37.10 | | 0 | | | 0 | |
| **FIRE AND EXPLOSION** | | | | | | | | |
| FIRE AND EXPLOSION HAZARD MODE SCORE = $S_{FE}$ | | 0 | | 0 | N/A | | 0 | N/A |
| **DIRECT CONTACT** | | | | | | | | |
| (1) Observed Incident | | =(0) | | =(0) | N/A | | =(0) | N/A |
| (2) Accessibility | | 2 | | 2 | N/A | | 2 | N/A |
| (3) Containment | | 15 | | 0 | c,d | | 0 | c,d |
| (4) Waste Characteristics/Toxicity | | 15 | | 0 | c,d | | 0 | c,d |
| (5) Targets | | | | | | | | |
| Population Within 1-Mile Radius | 4 | | 4 | | | 4 | | |
| Distance to Critical Habitat | 4 | | 4 | | | 4 | | |
| Total | | 8 | | 8 | N/A | | 8 | N/A |
| DIRECT CONTACT HAZARD MODE SCORE [(1)x(2)x(3)x(4)x(5)/21,600]x100 = $S_{DC}$ | | 16.67 | | 0 | | | 0 | |

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LEGEND

=(0)= Scored as zero, but method of score calculation does not include this value.
N/A = Nonapplicable.
a = No documentation of an observed release.
b = No demonstrated leakage from containment.
c = No documentation of the presence of reportable quantities of hazardous substances.
d = No documentation that Hammermill's injection liquor was a hazardous waste or present at the well.
e = Aquifer of concern is saline.
f = "Observed release" resulted from transitory conditions due to facility disturbance investigative personnel.

Hammermill had maintained that the Bass Island Formation should be considered a container under the HRS guidance, and that as such, the container should be considered as being sealed (score = 1) as of 1979 when PADER capped the well. EPA (9/83) responded that the capping of the well in 1979 did not negate the potential impact of past waste migration at this well or from other wells not yet identified in the area, the well was considered to have had no containment historically, and it was therefore assigned a score of 3.

Hammermill commented that documentation had not been provided to show that potentially hazardous substances are present at the Presque Isle site in amounts greater that reportable quantities, and therefore the toxicity/persistence and hazardous waste quantity rating factors should be scored as zero (EPA, 9/83). The agency responded that the results from the Renkis background well show levels of contaminants below those found at Presque Isle, the substances cannot be separated from the 1.1 billion gallons of injected pulping liquor, and therefore, a value of 8 had been assigned under these rating factors (EPA, 9/83). The site would be scored based on the presence of benzene and phenol rather than on lead, as it was originally scored (EPA, 9/83). Further, EPA noted that reportable quantities are required to score a site only when the total inventory of the substances in a facility is known, and this was not the case with the Presque Isle site (EPA, 9/83).

Hammermill suggested that if the aquifer of concern was the Bass Island Formation, then there were no targets at risk, because the aquifer is saline (EPA, 9/83). EPA (9/83) agreed that the aquifer of concern was the surficial aquifer, but because of the potential for fluids to rise from the Bass Island Formation to the surface at other wells, the surficial aquifer could potentially be affected. The results of these changes reduced the ground water route score from 28.57 to 20.51 (EPA, 9/83).

Hammermill felt that rainfall as assessed under the surface water route would act as a diluting agent rather than as a driving or leachate-generating mechanism (EPA, 9/83). According to EPA (9/83), the HRS does not provide for any beneficial effect purported to be due to the dilution of contaminants by rainfall, and EPA (9/83) thought that no change in scoring was warranted. Hammermill felt that the instructions for scoring the surface water pathway were not applicable to the Presque Isle site, based on the previous assertion that the containment rating factor should be assigned a value of one, because the formation had been sealed since 1979 (EPA, 9/83). EPA (9/83) noted that based on the history of the site, and the previous conditions at the site before remedial actions were taken, the assigned value of 3 was correct. EPA (9/83) revised the surface water score from 10.67 to 8.20 to account for the change in the toxicity/persistence rating factor from lead to benzene and phenol.

Hammermill commented that the factors used to score the air route pathway were invalid, because investigators had created transitory conditions when they opened the well to conduct sampling (EPA, 9/83). EPA (9/83) noted that (1) human health was at risk during the venting of the well, (2) Draeger tube sampling indicated that hydrogen sulfide was present when the problem at Beach No. 7 first became apparent, (3) measurements were made of the ambient air surrounding the well showing hydrogen sulfide gas was present, and (4) the HRS scores a release when the levels observed at, or in the vicinity of, the facility exceed background levels, regardless of the frequency of the release. During its review of the rating factors used for waste characteristics, a change was made to increase the original reactivity and incompatibility score from 0 to 3, because hydrogen sulfide gas is released when the brine comes into contact with water having a lower pH. This change increase the air route score from 56.67 to 66.67 (EPA, 9/83).

The original migration score for the Presque Isle site was 37.20. The net effect of these revisions to the HRS model raised the total score to 40.59 (EPA, 9/83).

3.51 Technical Meeting With Hammermill After Inclusion of Site in NPL (September 1983)

EPA, PADER, and USGS officials participated in a conference call to discuss the strategy for the September 22, 1983 meeting with Hammermill on remedial options. PADER attorney Howard Wein stated that Hammermill's attorney had indicated that it was willing to move in the direction of cleaning up rather than toward further litigation. The Hammermill attorney had suggested that the waste could be reinjected into deeper formations, but Mr. Click and Mr. Walker doubted this would be feasible (Walker-PADER, 9/12/83b). Mr. Click of the USGS felt that much of the evidence was circumstantial and that additional evidence on the areal extent of the waste was required before deciding on remedial actions. Mr. Click also felt that remedial actions should be designed to isolate the "superbrine" waste to prevent it from being forced into the shallow ground water by locating old wells, checking the composition of the well water, and sealing them (Walker-PADER, 9/12/83b).

John Walker of PADER felt that a well should be drilled on the Hammermill property to depressurize the waste disposal reservoir, to obtain a core of the reservoir, to obtain fluid samples, and to flow back wastes until the reservoir pressure was lowered to near the original pressure (Walker-PADER, 9/12/83b). Mr. Shoener of EPA felt that it was important to attempt to both (1) depressurize the Bass Island Formation by drilling a monitoring well, and (2) conduct a study of the Erie area to determine the extent of the problem, to identify and plug outlets, and to remedy any past problems (Walker-PADER, 9/12/83b).

The meeting between regulatory officials and Hammermill representatives concerned D'Appolonia's technical comments on PADER's recent report (Walker-PADER, 8/15/83). Hammermill agreed with the stratigraphy section of the report, but its representatives noted that the Bois Blanc Formation was not recognized when their injection permit was issued. Hammermill also stated that (1) D'Appolonia had discovered over 200 Erie County wells at which black water occurred in the Bass

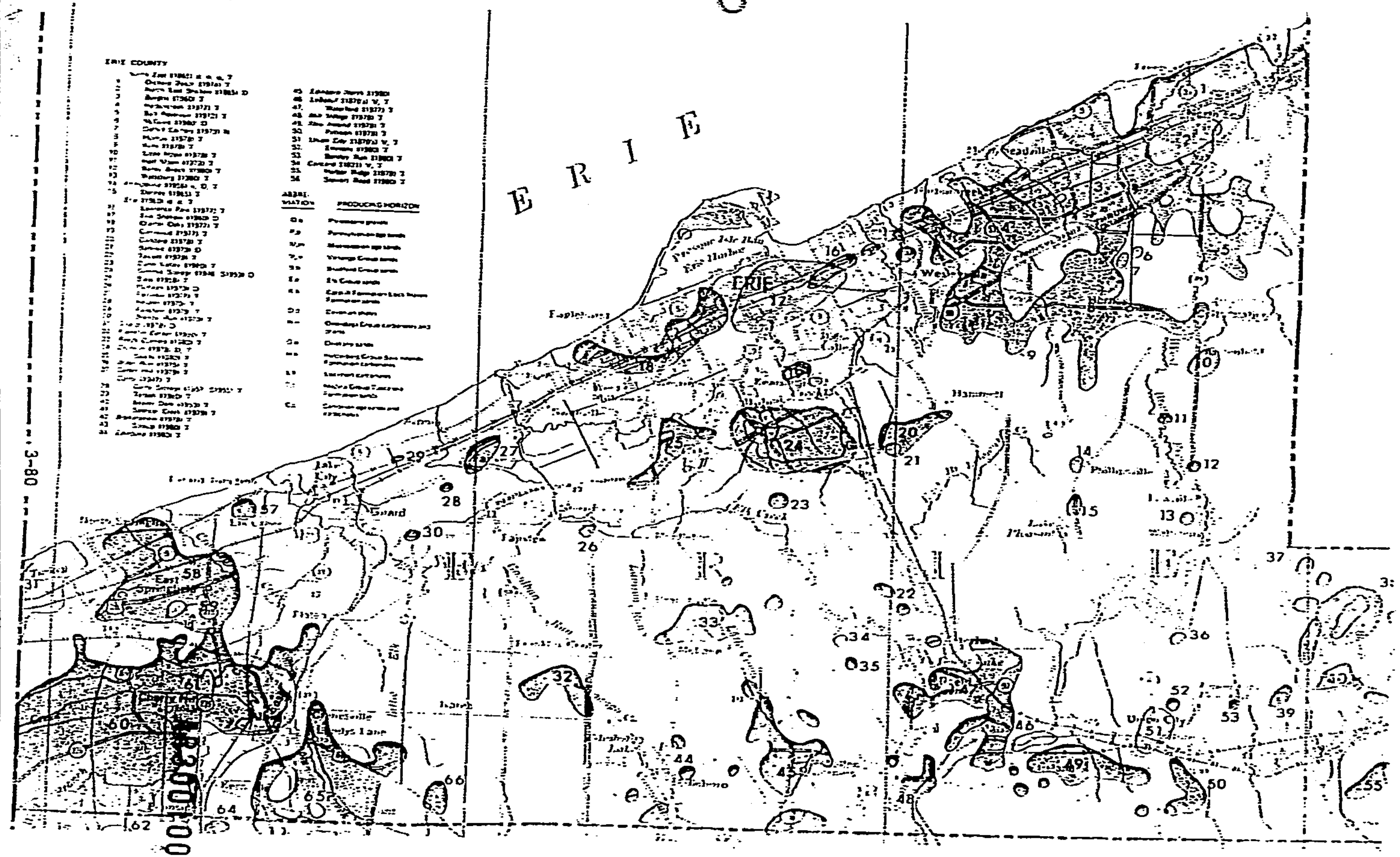


FIGURE 3-13
OIL AND GAS FIELDS IN ERIE COUNTY, PENNSYLVANIA
(PADER/Pennsylvania Geologic Survey, 1982)

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Island Formation (the wells were drilled between 1977 and 1979), (2) hydrogen sulfide was commonly encountered in the Summit field of Erie County (Figure 3-13) and locally in New York. Therefore, Hammermill concluded that black water in the Bass Island Formation should not be considered as unusual (Walker-PADER, 9/22/83).

Hammermill maintained that the cause of tree mortality could be related to high water or to the seep, and seepage would have been diluted by rainfall. Hammermill also maintained that in the maximum wellhead pressure of 65 psi, the contribution of the Devonian gas shale pressure should be considered, because a 105-psi gas pressure was observed at the well after it was completed as a producing gas well (Walker-PADER, 9/22/83). Hammermill also stressed that the concentrations of naturally occurring hazardous substances in the Lockport Formation fluids were more hazardous than substances in the Bass Island Formation fluids (Table 3-3) and that the Bass Island Formation has a high natural gas potential, as noted by Kelly and McGlade (1969). D'Appolonia also noted that gas has a higher coefficient of permeability, suggesting that the hydrogen sulfide gas might have moved from the Lockport Formation through the Salina evaporites and into the Bass Island Formation (Table 3-3).

Hammermill commented that lignin was not present in the Bass Island Formation at the Beach No. 7 well, and filtering was an irrelevant issue, since the tannin-lignin measurement was higher for the Renkis well. Hammermill suggested that the results were an analytical artifact created by interference from a high calcium content, and the method employed was not applicable to these brines (Walker-PADER, 9/22/83). When Hammermill applied specific ultraviolet methods to the analyses, amounts of tannin-lignin were found at the limits of detection, indicating that these compounds were not truly present (Walker-PADER, 9/22/83). Additionally, acetate/formate ratios observed at the Beach No. 7 well were the opposite of ratios expected for the hardwood process employed by Hammermill (Walker-PADER, 9/22/83).

James Rogers, Hammermill's attorney, indicated (1) the issue had grown to a broader issue concerning potential public health problems, (2) 30,000 wells were similarly involved in underground injection in Texas and Oklahoma (presumably meaning without incident), (3) a lot of information was needed for a conclusive solution, and (4) there was no present risk to the environment and no danger to the public health (Walker-PADER, 9/22/83). Mr. Shoener raised the issue of installing a monitoring well to depressurize the formation (Walker-PADER, 9/22/83). Mr. Click, however, felt that this could be a very expensive undertaking, because many wells would be needed to determine the pressure gradient for the system. Mr. Click also thought that the older deep wells in Erie County should first be examined, and nearby water wells should be analyzed before drilling any wells (Walker-PADER, 9/22/83).

Mr. Rogers noted that $150,000 would be required for each monitoring well to "satisfy scientific curiosity, one well would not satisfy EPA, and [the investigation would result in an] endless program of drilling wells" (Walker-PADER, 9/22/83). These same objections were later formally stated by Rogers (HML, 10/20/83). Rogers also questioned the idea of depressurizing the formation, allowing the flow-back and treatment of the waste (Walker-PADER, 9/22/83). Hammermill noted that it was possible to have dendritic flows of the pulping liquor based on variations in formation porosity and permeability as noted in the Wayne Street and Vincent High School wells (Walker-PADER, 9/22/83).

3.52 Further Comments on PADER's August 15, 1983, Report (September-October 1983)

In addition to the technical comments made above, internal Hammermill correspondence obtained by Versar (Andrews-HML, 9/8/83) was later incorporated into a document that rebutted the PADER August 15, 1983, report "Beach 7 Well Problem, Presque Isle State Park and Its Connection with Hammermill's Waste injection Wells" (Walker-PADER, 8/15/83). Hammermill's general observations and criticisms were as follows:

TABLE 3-3
COMPOSITIONS OF BRINES IN THE BASS ISLAND AND
LOCKPORT FORMATIONS AT THE PRESQUE ISLE BEACH NO. 7 WELL
(Andrews-HML, 10/26/83)

| FORMATION | THICKNESS (FEET) | REMARKS | | | | |
|---|---|---|---|---|---|---|
| DEVONIAN STRATA | 1480 | OVERLYING SHALLOW DEVONIAN SHALE COMMERCIAL GAS PRODUCTION STRATA | | | | |
| BASS ISLAND | 60 | | TDS (g/ℓ) | Cℓ (g/ℓ) | pH | $H_2S$ (mg/ℓ S) |
| | | PennDER | — | 177 | 6.4 | 236 |
| | | USGS | — | 180 | — | — |
| | | D'APPOLONIA | 266 | 186 | 6.6 | 152 |
| | | HYDROSTATIC PRESSURE: FLOW OBSERVED AT SURFACE | | | | |
| SALINA | 360 | NO NATURAL GAS PRODUCTION | | | | |
| LOCKPORT | 350 | | TDS (g/ℓ) | Cℓ (g/ℓ) | pH | $H_2S$ (mg/ℓ S) |
| | | PennDER | — | — | 5.8 | 941 |
| | | USGS | — | — | — | — |
| | | D'APPOLONIA | 208 | 132 | 5.6 | 312 |
| | | HYDROSTATIC PRESSURE: FLOW OBSERVED AT SURFACE | | | | |
| MEDINA | | UNDERLYING COMMERCIAL GAS PRODUCTION STRATA | | | | |

DEEP SUBSURFACE CONDITIONS AT PRESQUE ISLE BEACH NO.7 WELL

1. The report was prepared by one person, without peer review or input from other experts.

2. The report contained many innuendos, suppositions, and proposed happenings, and it tended to set forth a hypothesis in one section and then proceed in the next section as though the original hypothesis were a proven fact.

3. The original theory of a fault or crack connecting the injection wells to the Beach No. 7 well had not changed; only the suggestion that Hammermill had violated its permit had been added.

4. The conclusion of the report seemed to be directed more toward making a case in point against underground injection than to expressing concern for a superfund-type situation posing an immediate threat to the environment.

5. There was no discussion of any remedial action, even if the truth of the hypothesis was proven (Andrews-HML, 9/8/83).

Hammermill's specific comments to the PADER report (Walker-PADER, 8/15/83) were as follows:

1. There were no data on the fresh ground water available at the Presque Isle site for comparison.

2. Tree kills at Presque Isle were investigated by Nichols (PADER, 8/7/81) who concluded that there was no evidence of a phytotoxic chemical actively stressing the vegetation, and tree mortality appeared to be associated with low elevation and abnormally high water levels.

3. On the color connection, "black liquor" is an industry term, and the color of the pulping liquor was actually reddish brown.

4. Walker (PADER, 8/15/83) concludes that welldrillers in the 1910 era kept accurate records, but he excuses Mr. Carrol and Envirogas for inaccurate records and inexperienced drillers, and he misreads Carrol's letter by ignoring the statement that "in some cases this [black water in the Bass Island Formation] could be possible" (Andrews-HML, 9/8/83).

At this point, Andrews (HML, 9/8/83) emphasized that there was a certain amount of circularity in Walker's (PADER, 8/15/83) arguments. In refuting the well logs indicating the presence of black water in the Bass Island Formation, which were cited in the D'Appolonia interim report

(HML, 3/83), Walker (PADER, 8/15/83) went to great lengths to establish that the Lockport Formation fluids could invade the Bass Island Formation via unplugged, surface plugged, natural fractures, faults, and so forth. Andrews (HML, 9/8/83) noted that this statement established Hammermill's contribution to the Bass Island Formation as being insignificant, especially when credence is given to Walker's (PADER, 8/15/83) insistence on horizontal and vertical cracks, faults, and so forth. Andrews felt that if black water, sulfur-bearing wastes, or natural communication between formations is available, the source of the wastes would make little difference, and that it was an example of Mr. Walker using only the information that served his theory (Andrews-HML, 9/8/83).

According to Andrews (HML, 9/8/83):

1. Walker (PADER, 8/15/83) presumes to know what "prudent road engineers" would have done in 1924, but Andrews felt that the assorted junk found while plugging the well was probably representative of the work done during that time.

2. The poor job of plugging the well was only sufficient to hold back the artesian flow for 30 years.

3. Road improvements in the 1950s bypassed this area of the park.

4. The April 1968 blowout did not last for weeks, as Walker (PADER, 8/15/83) suggests, but only from April 14 to 30.

5. Walker (PADER, 8/15/83) equates the seep rate in 1982 with that in 1979, thereby indicating that there was no decrease in flow, which would be expected if the injection program were the driving force behind the flow at Beach No. 7.

Versar feels it is important to note that Walker's (PADER, 8/15/83) statement on the seep rate is qualitative. Furthermore, Andrews (HML, 9/8/83) and later D'Appolonia (HML, 10/27/83) take this comment concerning 1979-1982 flow rates out of context when they attempt to suggest that no decline in pressure occurred between 1979 and 1982. The flow rate as originally measured was 411 gpd (Walker-PADER, 4/5/79), but it had declined substantially to 288 gpd by May 3, 1982 (Walker-PADER, 12/16/82). Again, flow rates do not necessarily indicate a decline in formation pressure.

Andrews (HML, (9/8/83) continued comments with the following: Referring to Walker's (PADER, 8/15/83) hypothesis that the "black gunk" could not move through the Bass Island Formation unless a very open, high-permeability fracture zone were present, Andrews asks for the reason why the seep did not take place sooner than 1970, for the locations of the other seeping wells, and for the means by which the pressure be maintained over an 11-year period. D'Appolonia (HML, 10/27/83) suggested that this "black gunk" never was in the formation; instead it was a reaction product created by interaction between formation fluids and the iron well bore.

Andrews objected to Walker's suggestion that the Bass Island Formation in the Erie area was "dry" (i.e., contained no economic quantities of oil or natural gas) because of its low porosity and permeability, and Andrews referred to recent Vinyard Oil and Gas News releases that suggested major oil and gas finds in Erie County (Andrews-HML, 9/8/83). Andrews' comment was later supported by the discovery of oil and gas in the Bass Island Formation near Lowville, Pennsylvania, with natural flows of 15 million cubic feet of gas and 30-40 gallons of oil per hour (Andrews-HML, 6/30/86).

Andrews (HML, 9/8/83) noted that Walker (PADER, 8/15/83) objected to using radial flow models in the permitting process and favored an extensive pre-permit drilling program to evaluate all the possibilities of waste fluid leaks from the waste disposal reservoir and the drilling of monitoring wells to determine the extent and pattern of waste fluid movement. Andrews commented that the only way to disprove the theory would be to have an endless coring adventure. Andrews felt that Mr. Walker was opposed to underground injection and was using Hammermill's injection program to prove his point. According to Andrews, the costs of such a pre-permit drilling program would make these projects totally impractical (Andrews-HML, 9/8/83).

Andrews (HML, 9/8/83) also made the following comments:

1. In Walker's refutation of the artesian flow model presented in D'Appolonia's report (HML, 3/83), Walker neglects the great amount of time required for the Bass Island Formation to assume its natural head.

2. Mr. Walker was mistaken in saying that vascular plants cannot produce tannin-lignin, acetate, formate, and resin acids.

3. The Bass Island Formation is under sufficient pressure to rise to the surface in adjacent Chatauqua County, New York.

4. Walker (PADER, 8/15/83) continues to misread the reports by Brown concerning the presence of titanium dioxide and other paper additives. Andrews (HML, 9/8/83) said Walker either would not listen, does not understand the reasoning, or does not want to understand.

Mr. Saylor (HML, 9/1/83), formally of the Erie Health Department, also commented on many of the same points, and he added that (1) Walker is incorrect in writing that the Erie County Health Department received complaints of a "foul smelling seep of black water," because he recollected that the complaints were about raw sewage or partially decomposed sewage leaking or being placed on the ground. The water was not particularly black or foul smelling, and the original purpose of the investigation was to determine if the seep was sewage.

Versar would like to note the following: Mr. Saylor's contention that the fluid was not particularly black or foul smelling in the early 1970s (Saylor-HML, 9/1/83), when considering Martz (PADER, 12/7/78) observation that an odor problem had become more intense over 1978, may indicate that this problem developed during the early 1970s, and it was not present before then. This could suggest that Walker's (PADER, 8/15/83) assertion that the odor became more apparent as the wastes reached the Beach No. 7 well during the late 1970s may be correct. Conversely, this might only indicate that the flow of fluid through the annulus had only recently disturbed the equilibrium surrounding the borehole, and the reaction between borehole and brine was only just beginning in the early 1970s. In either case, the observations of increasing odor and "blackness" do not support the idea that the well had been flowing before 1970.

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Saylor (HML, 9/1/83) also felt that Walker's assertion that the 4 1/2-inch, elbow-shaped drain pipe found jammed over the 3-inch, clay-plugged casing was to used to divert gas is questionable. Saylor questions why road builders would install a drain pipe to divert flows of gas from a plugged casing, and he felt that it was more likely that the drain pipe was used to divert flows of fluids from the 6 1/4 to 8 5/8-inch annulus. Versar discussed this matter with Mr. Saylor during a discussion with Hammermill officials. Saylor maintained the following: Flows of gas would not affect the overlying road. However, fluids accumulating during the winter would freeze below the grade, causing the road to buckle. Therefore, there are sound engineering reasons for interpreting the purpose of the drain pipe as a conduit for fluids, but there is little reason to interpret that the pipe was to vent gas (Saylor, personal communication, 12/8/83).

Saylor (HML, 9/1/83) made the following points:

1. Outdoor privies would have masked odors from the seep. Since these privies were torn down in the mid-1970s, this would make odors coming from the seep seem more prevalent.

2. Walker's (PADER, 8/15/83) discussion of variability in chemical analyses as evidence of the presence of man-made material does not include a consideration of the variability in test methods, and natural sample variability.

3. Walker (PADER, 8/15/83) states in several places throughout the report that the Bass Island and Bois Blanc formations are poor producers of hydrocarbons. However, Walker attempts to blame the sour gas problem at the Memorial Technical High School well on the presence of pulping wastes, ignoring the fact that the well produces large quantities of natural gas.

D'Appolonia (HML, 10/27/83) incorporated virtually all of these comments in much greater detail on a point-by-point basis into its "Technical Review of the August 15, 1983 PADER Report." D'Appolonia also made the following points (HML, 10/27/83):

1. Flow volumes before 1979 are only as accurate as the estimates of flow rates.

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2. Noxious odors would not necessarily have been present during the drilling of the well in 1910, because significant contact with the well casing was required to lower the pH, and the fluid did not give off foul-smelling odors during the plugging and testing project in 1982.

3. The description of fluids "spewing out of the well" was inappropriate to flows of around 1 quart per minute and, this would not create difficulties for experienced drillers.

4. The report (Walker-PADER, 8/15/83) states that injection zones can be considered to be approximately 20 feet thick. However, the report also accuses Hammermill of inducing horizontal and vertical fractures, and therefore the injection zone would not necessarily be limited to only 20 feet.

5. Walker states that the Bass Island Formation at Beach No. 7 contains <u>no</u> producible hydrocarbons. However, the well was observed to produce natural gas, and many of the organic contaminants would be expected to occur naturally at the concentrations found if natural gas (hydrocarbon compounds) were present.

D'Appolonia is highly critical of Walker's (PADER, 8/15/83) treatment of lineaments:

1. The report implies that D'Appolonia's lineament map shows fracture traces. However, D'Appolonia (HML, 10/27/83) correctly notes that all lineaments are not necessarily fractures.

2. Walker refers to an east-west lineament as a direct indicator of fractures in the Bass Island Formation, but Walker also states that fracture systems observed at the surface may be connected with or correspond in location to the fracture systems of other formations at depth.

D'Appolonia (HML, 10/27/83) objects to Walker's (PADER, 8/15/83) assertion that low porosity and low permeability can be inferred from visual observation of cuttings, stating that it is impossible to <u>quantify</u> porosity and permeability based on examination of cuttings. Versar feels that D'Appolonia (HML, 10/27/83) takes this comment out of context. True, it is impossible to <u>quantify</u> porosity and permeability from cuttings. However, cuttings often show evidence of fractures or fracture fillings, and it is standard petroleum industry practice to record the presence of these features as qualitative evidence of fracturing within the reservoir.

D'Appolonia (HML, 10/27/83) also criticized Walker by making the following comments:

1. Walker's assertion that displacement of connate brines is difficult, noting that this is common in enhanced recovery procedures for oil fields.

2. Walker (PADER, 8/15/83) calculates the size of the waste-invaded area to be 4.8 square miles, but this is equivalent to a radial distance of only 1.24 miles. If one discounts the radial theory of flow, then Versar notes that by using Walker's calculated volume, the width of this zone must be only a mile or so, the zone is pointed directly at the Beach No. 7 well, and it does not continue east of the Hammermill injection wells.

D'Appolonia (HML, 10/27/83) also notes that they were unable to respond to Walker's suggestion that an elongate zone of abnormally high salinity northeast of the Erie City limits (Figure 3-14) may be the result of displacement of Bass Island brines, because that data was not made available to Hammermill. Versar feels it is important to note that this area is not necessarily related to the displacement of brines from injection pressure. There are many other areas in Erie County with similar salinities, and these areas correspond to oil field areas, probably because of the brines brought to the surface during routine drilling activities (Compare Figure 3-14 with Figure 3-13).

D'Appolonia (HML, 10/27/83) notes that Walker (PADER, 8/15/83) ignores the evidence cited in their report (HML, 3/83) when he writes (on page 35 of the Walker report) that "there is no evidence from thousands of wells drilled in Pennsylvania, western New York, and Ontario which indicates that the Bass Island Formation is overpressurized and capable of pushing water to the surface when penetrated." Versar notes that qualitative fill-up data were well documented in the Dow feasibility study (HML, 11/19/62)

AR300110

PROVISIONAL DATA
SUBJECT TO REVISION

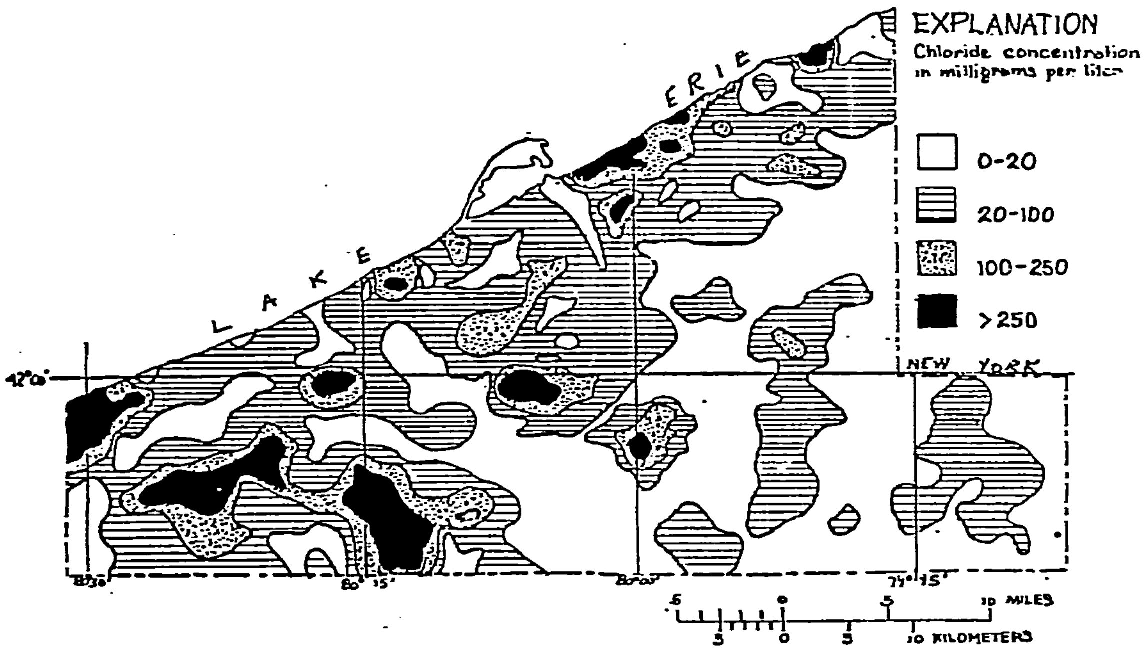


FIGURE 3-14
DISTRIBUTION OF CHLORIDE CONCENTRATIONS (SALINITY)
IN GROUND WATER FROM WELLS SAMPLED IN ERIE COUNTY, PENNSYLVANIA

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Versar is concerned that Walker mentions Ontario in this statement, but he does not include the information on sulfurous brines and flowing artesian conditions in the Bass Island Formation in Ontario, which was outlined in a letter to him (Trevail, 8/5/83). This letter (Trevail, 8/5/83) was marked as being received by his section on August 10, 5 days before the Beach No. 7 well problem report (Walker-PADER, 8/15/83) was issued.

The D'Appolonia (HML, 10/27/83) criticism continued with the following comments: The fluid measurement at the Renkis well was only a single measurement. Therefore, it cannot be assumed to indicate the natural hydrostatic fluid level. This is true. However, Mr. Shoener (personal communication, 3/18/87) informed Versar that only a single measurement was possible, because the driller would have charged approximately $10,000 a day for down time to make this observation. This fact clearly establishes the reason why only qualitative evidence is recorded on drillers logs. Unless the drillers are specifically interested in hydrostatic levels (and there is little reason for them to be so interested), there are no economic incentives to make other than qualitative references to fluid fill-ups from the Bass Island Formation or other formations.

D'Appolonia (HML, 10/27/83) also takes issue with Walker's (PADER, 8/15/83) statement that the oil and gas productive Bass Island Formation in Chatauqua County, New York (immediately adjacent to Erie County), is an underpressured reservoir. D'Appolonia (HML, 10/27/83) indicates that Lou Nalbone, President of the J&L Oil and Gas Corporation, informed D'Appolonia that both oil and brine have flowed to the surface from the fractured Bass Island reservoir in Chatauqua County.

D'Appolonia (HML, 10/27/83) also made the following objections to many of Walker's (PADER, 8/15/83) statements regarding the hydrogeology of Hammermill's injection program:

1. No initial observations were made. Therefore, there was no basis to conclude that natural formation pressures were less than 500 psi.

2. The flattening of the injection pressure curve could indicate that other phenomena besides a leaking fault were involved.

3. The Hagen-Pouseuille equation applies to flow in a smooth cylindrical pipe. Therefore, it is not applicable.

4. Kleeman's calculations were based on unrealistically high injection pressures, and no calculations had been presented by EPA to model the pressure decline following the cessation of injection at the Hammermill wells.

5. Computer analyses by Dr. Koederitz had not been made available, so D'Appolonia could not discuss them.

D'Appolonia (HML, 10/27/83) also made the following comments:

1. They had located over 200 well logs showing the occurrence of black water in the Bass Island Formation or its stratigraphic equivalents.

2. Walker's assertion that the Envirogas well logs were inaccurate was not born out by these logs, because several other drilling companies had also noted the same occurrence.

3. Walker was incorrect in stating that sulfides were present in the pulping liquor; sulfite was present.

4. Walker (PADER, 8/15/83) presents no data to support his assertion that reactions between the pulping liquor and native brine would increase the concentrations of natural constituents in the brine.

D'Appolonia (HML, 10/27/83) defends at length its data on artesian flow, the presence of artesian conditions in the Oriskany Formation, and the reasonableness of extrapolating data for the Oriskany flows in Erie County to the flows from the Bass Island Formation. Since the Oriskany Formation is a porous sandstone that directly overlies the Bass Island Formation in some locations in Erie County, it is reasonable to assume that where the porous Oriskany Formation overlies porous zones of the Bass Island Formation, the pressure inherent in the Oriskany Formation would be transmitted to the Bass Island Formation.

3.53 Development of the Draft Remedial Action Master Plan (November 1983)

SRW Associates, under subcontract to NUS Corporation, prepared a Draft Remedial Action Master Plan (RAMP) for the Presque Isle site. The RAMP (SRW-EPA, 11/83) noted two principal environmental concerns: direct human exposure to gaseous and liquid wastes from uncontrolled discharges, and potential contamination of surface and ground water by pressure flow through fractures, gas and oil wells, or other pathways. The RAMP (SRW-EPA, 11/83) also identified initial remedial measures (IRMs) and long-term remedial measures for the site.

Initial remedial measures are warranted to mitigate the potential for human contact with the wastes, and they are determined based on the amount and form of the hazardous substances, the hazardous properties of the waste, fire and explosion threats, and others (SRW-EPA, 11/83). SRW (EPA, 11/83) suggested two specific IRMs:

1. Notify drillers in the Erie area that wastes under pressure may be encountered when drilling through the Bass Island Formation and that provisions should be made to control liquid and gas discharges.

2. A contingency plan should be developed for the prevention and sealing of any discharge that may occur from the Bass Island Formation.

Long-term remedial measures included (1) pressure reduction of the Bass Island Formation to stop or slow migration of the contaminants, (2) removal or treatment of the contaminated ground water and soils surrounding the Beach No. 7 well and any other wells that may be identified in subsequent investigations, (3) sealing and plugging of waste discharges from the Bass Island Formation that could lead to human contact, degradation of surface water or ground water or the release of hazardous wastes (SRW-EPA, 11/83).

The RAMP also proposed a Remedial Investigation/Feasibility Study (RI/FS) that would have cost $471,000, excluding the analytical costs

(SRW-EPA, 11/83). The tasks of the proposed RI/FS were in many respects, very similar to studies that had been already completed: (1) Sampling and analysis of ground water at the Beach No. 7 well, (2) water well location and sampling near the oil and gas wells within a 5-mile radius of Erie, and (3) analysis of discharges from the Bass Island Formation if such discharges were observed during the RI (SRW-EPA, 11/83). The fourth aspect of the RI was different from previous studies and was to install a deep monitoring well on the Hammermill property to sample Bass Island fluid and to observe formation pressures. In addition, arrangements would have been made to sample other wells in the vicinity that might penetrate the Bass Island Formation during the RI (SRW-EPA, 11/83).

Possible remedial actions identified as being appropriate to the Presque Isle site included (1) pressure reduction of contaminant-bearing formation fluids in the Bass Island Formation, (2) removal of contaminated soil or sediment, (3) removal of contaminated ground water from the Presque Isle area, (4) sealing or plugging of any discharge or source of contaminant release from the Bass Island Formation, and (5) shallow ground water treatment (SRW-EPA, 11/83).

The RAMP (SRW-EPA, 11/83) recognizes that long-term remedial measures would not be appropriate if most of the injection pressure has dissipated at the disposal location or if the substances are adequately contained. In addition to residual pressure reduction, the RAMP also recognized that "no action," or a "minimum action" might be appropriate in addressing both the environmental and financial consequences of such a decision. Offsite source control measures need to assess the contribution to an air, land, or water problem; the extent of migration; and if continued migration might pose a danger to public health and welfare, or to the environment (SRW-EPA, 11/83).

### 3.54 Hammermill Decides Not to Challenge the Inclusion in NPL (December 1983)

Hammermill had considered petitioning for judicial review of the rulemaking underlying EPA's placement of the Presque Isle site on the NPL

(Brown-HML, 12/6/83). Hammermill informed EPA (Brown-HML, 12/6/83) that it had decided not to challenge the NPL, and although they felt the U.S. Court of Appeals would look favorably on their position, they felt that the issue could be resolved through the cooperation of EPA, PADER, and Hammermill. Brown (HML, 12/6/83), however, indicated that they would be willing to go to court if EPA seeks cost recovery.

3.55 Further Findings by Academic Consultants and the USGS (May-July 1984)

Dr. Koederitz (UMR/EPA, 5/8/84) submitted the results of 25 sophisticated reservoir simulations to determine the influence of fractures and directional permeability and of perimeter plugging scenarios on pressure drive at the Beach No. 7 well. This finite element model (discussed in Section 6.0) found that pressures sufficient to cause the Beach No. 7 well to flow until 1984 could only be produced under a perimeter plugging scenario employing an east-west directional permeability and a 20-foot thick injection reservoir (Koederitz-UMR/EPA, 5/8/84 and Shoener-EPA, 10/85).

Not even the perimeter plugging scenarios could account for the observed flows at the well if a 75 foot reservoir were available for injection (Koederitz-UMR/EPA, 5/11/84). This model is more fully discussed in Section 6.0 of this report.

EPA asked Dr. Arthur Hounslow of Oklahoma State University (OSU) to undertake a literature search to determine (1) feasibility of pore plugging reactions between the Bass Island Formation, the formation fluids, and the injection liquor, and (2) whether the organic compounds in the formation fluids of the Beach No. 7 well could be naturally occurring petroleum hydrocarbons.

Bacterial degradation and the differential solubility of the organics present in petroleum complicate the question of whether the organic fraction in the samples is natural or waste derived (Hounslow-OSU/EPA, 6/30/84). Examination of the analyses of the organics

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in the seep and the Lockport and Bass Island formations failed to reveal an unequivocal origin:

1. The wide variety of hydrocarbons in the seep samples and a noticeable lack of cyclic alkanes suggest a refined petroleum source, but the great diversity of hydrocarbons is impossible to explain.

2. The organic makeup of the Lockport Formation samples suggests a petroleum origin. However, the presence of N-butyl benzene sulfamide could not be explained.

3. Bass Island fluid samples were similar to the seep (but contained many fewer unsaturated compounds). The dominance of C7-C19 hydrocarbons and the presence of disulfides suggest a refined petroleum source (Hounslow-OSU/EPA, 6/30/84).

Dr. Hounslow (OSU/EPA, 6/30/84) suggested a model involving biological action to explain the composition of the seep. Hounslow noted, however, that even this model is very difficult to support unless oxygen is introduced to the formation. In view of the very low concentrations of organics in the samples, the anomalous compounds in all three samples, and the suggestion that a refined petroleum source may be present, Versar feels that contamination could have resulted from either improper sampling of well water or the presence of pipe dope or of other materials, and the contamination may be contributing to the compounds observed.

Dr. Hounslow recognized four possible reactions that may have contributed to the reductions in porosity and permeability needed to result in the perimeter pore-plugging required by Koederitz's models: (1) calcium lignin sulfonate precipitation, (2) gypsum precipitation, (3) iron sulfide precipitation, and (4) dedolomitization. Several wells and cores would be necessary to establish if any or all of these reactions were occurring (Hounslow-OSU/EPA, 6/30/84).

Dr. Cooper-Driver of Boston University (BU) reanalyzed data from the the Renkis well and Beach No. 7 well for lignins and associated compounds (Cooper Driver-BU/EPA, 6/4/84). Much of these results have already been discussed in Section 3.35 concerning the Renkis well. Niklas (Cornell/EPA, 7/84) incorporated the results into his report and had the following conclusions:

1. The occurrence of lignin from a petroleum source could not be ruled out, but it would have had to migrate from other formations.

2. Great variation in the results of chemical analysis precludes meaningful comparisons between the samples.

3. The data are insufficient to resolve if the lignins are naturally occurring.

4. Currently available analyses are incapable of resolving the issue.

5. Continued observation might resolve these issues, but due to the complexity of the system, unambiguous results may not be possible (Niklas-Cornell/EPA, 7/84).

Dr. Garry Erlich, Chief of the USGS Microbial Ecology of Groundwater Project, examined the data from D'Appolonia (HML, 3/83) and Walker (PADER, 8/15/83) for the influence of microbial reactions on the pulping liquor. Dr. Erlich had several conclusions:

1. The pulping liquor would have been a suitable source of nutrients for sulfate-reducing bacteria, but not the only source.

2. The reversal of the 10:1 acetate to formate ratio in the pulping liquor found in the brine samples might show natural conditions, especially since acetate and formate should decay at about the same rate due to their similar atomic structure.

3. The ratio reversal should not be due to decomposition or dilution.

4. Methanogenesis would remove acetate and formate from solution. Therefore, their absence does not preclude the possibility that the seep was derived from the pulping liquor (Erlich-USGS, 3/16/84).

3.56 Hammermill Synthesizes Neutracel I for Analysis (August-September 1984)

Hammermill submitted a letter report to EPA that included detailed chemical analyses of a sample of Neutracel pulping liquor generated by the Institute of Paper Chemistry according to the procedures used by Hammermill in the 1960s and early 1970s (Rogers-HML, 9/7/84). IT Corporation (formerly D'Appolonia before 1984) compared the data with the composition of the samples from the Beach No. 7 well and the Renkis well (D'Appolonia/IT-HML, 8/31/84).

Notably, many compounds such as methylene chloride, assorted acid and base/neutral compounds present in the pulping liquor were not found in the seep or the Bass Island Formation. In addition, many constituents of the seep, such as titanium dioxide, lithium, boron, strontium, nitrogen-ammonia, benzene, high molecular weight polynuclear compounds, aromatic hydrocarbons, alkenes, ketones, cyclic hydrocarbons, and organosulfur compounds, were not present in the Neutracel sample (D'Appolonia/IT-HML, 8/31/84). Furthermore, a comparison of the ratios of key indicators does not suggest that the pulping liquor had reached the Beach No. 7 well (D'Appolonia/IT, 8/31/84). The implications of these data are discussed in Section 5.0 of this report.

3.57 East High School Well Investigation (September 1984-March 1985)

On September 12, 1984, USGS and Hammermill representatives conducted sampling of a gas well being drilled at East High School, which is located five blocks from the Hammermill Paper Company facility. Arrangements were made with the L&K Drilling Company to collect a sample from the Bass Island Formation. Water and soap were not added to the well until after the water sample was collected (Squillace-USGS, 9/19/84).

The Oriskany Formation was described as a thin, quartz sandstone (Squillace-USGS, 9/19/84). This formation is absent in the nearby Hammermill injection wells. The sandstone that the USGS geologists identified as being from the Oriskany Formation is probably the equivalent of the Bois Blanc Formation, which was recognized in the Hammermill wells by Walker (PADER, 8/15/83) and contains zones of Oriskany-equivalent or Oriskany-derived sands. Jack Wright of D'Appolonia/IT observed the drilling and the sampling, and he notes that the USGS was not aware of the Bois Blanc Formation (Andrews-HML, 3/7/85).

No hydrogen sulfide gas was detected during drilling, and Draeger tubes also did not indicate the presence of this gas (Squillace, 9/19/84). Based on the presence of lignin (found by using sophisticated ultraviolet methods) and the acetate/formate ratio, Hammermill felt that their pulping liquor had reached this site (Starfield-HML, 3/8/85). In view of this, Hammermill felt that the lack of hydrogen sulfide gas at this location was quite significant (Starfield-HML, 3/8/85). The acetate/formate ratio at the East High School well was 13:1, on the order of the expected 10:1 ratio for the hardwood pulping liquor.

The same organic "fingerprint analysis" that USGS performed on the Renkis well and Beach No. 7 well were run on this sample. The fingerprint pattern evident in the Beach No. 7 well and seep was completely absent in the East High School well (Nottingham-USGS, 10/11/84). Chemical data from this well are more fully discussed in Section 5.0 of this report.

### 3.58 Review of EPA Documents and Revised Neutracel Results (March 1985)

In addition to discussing the East High School gas well, Andrews (HML, 3/7/85) includes a technical review of EPA documents obtained under the FOIA. These documents include reservoir modeling by Koederitz, and lignin analyses by Dr. Cooper-Driver.

Hammermill felt that Dr. Koederitz' models agreed with its conclusion, which was as follows: When the permeability was high enough to allow the pulping liquor to migrate to the Beach No. 7 well, the pressure would not buildup to sufficient levels to cause flow. Conversely, when the permeability was low enough to allow a pressure buildup, the chemical constituents would not reach the well (Andrews-HML, 3/7/85).

Other Koederitz scenarios were dismissed by D'Appolonia, because they required unrealistically high injection pressures in the model. They do not specifically discuss the perimeter pore-plugging models (Andrews-HML, 3/7/85). Versar attempted to verify these conclusions by examining the model inputs supplied to Hammermill under the FOIA. However, Versar was unable to locate this information in the FOIA files, the modeling files, and Dr. Koederitz' files from EPA Region III. Dr. Koederitz informed Versar that the raw data had been mailed directly to Mr. Norman Howard at NUS (personal communication, 3/25/87). However, Mr. Howard (personal communication, 3/26/87) informed Versar that the data had been sent directly from Dr. Koederitz to EPA Region III.

Hammermill generally agreed with Dr. Cooper-Driver that samples from the seep, the Lockport and the Bass Island formation fluids from the Beach No. 7 well and Bass Island Formation fluids did not contain tannin-lignin (Andrews-HML, 3/7/85). Hammermill also pointed out that although lignin is generally insoluble, the purpose of the pulping process is to make this compound soluble, thereby freeing the fibers in the hardwoods. Hammermill added that if the lignins did bind to sediment as discussed, it is unlikely that they would have migrated to the Beach No. 7 well in any case (Andrews-HML, 3/7/85).

Hammermill also submitted a reanalysis of the Neutracel pulping liquor previously generated by the Institute of Paper Chemistry to account for spurious levels of chloride, methylene chloride, and toluene reported by ETC Laboratories. All of these compounds were present only at trace levels in the reanalysis of the pulping liquor sample. Therefore, regarding the Beach No. 7 well, Hammermill stated that (1) chloride cannot be used to indicate the presence or absence of pulping liquor in Bass Island fluids, (2) methylene chloride cannot be used to establish the presence of the pulping liquor, and (3) toluene cannot be used to establish the presence of the pulping liquor, since it occurs naturally (Andrews-HML, 3/7/85).

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### 3.59 EPA Moves to Delist the Site from the NPL (August 1984-October 1985)

EPA Region III prepared a status report on the Presque Isle site which contained the following conclusions:

1. The occurrences at Beach No. 7 were unusual events, and previous studies had failed to conclusively establish the source of the seep.

2. Studies of the surrounding area had failed to locate any other problems associated with the discharge of hazardous fluids from the Bass Island Formation.

3. The hydrogen sulfide only built up to dangerous levels when the fluid was contained.

4. The principal health threat was to individuals near oil and gas wells during drilling (Shoener-EPA, 8/84).

The report recommended adoption of the following initial remedial measures identified in the RAMP:

1. Notify local drillers of the potential for high formation pressures and hydrogen sulfide gas.

2. Installation of a program to closely monitor new oil and gas wells during drilling was the appropriate measure in this situation.

3. The installation of deep monitoring wells was not necessary based on the currently available information (Shoener-EPA, 8/84).

EPA next attempted to determine if the site could be delisted under the current guidelines. EPA Region III recognized that the Presque Isle site was an unusual NPL site, originally listed because of the possible link with the Hammermill injection program. Remedial investigations by PADER, EPA, USGS, and academic consultants had only been able to establish a reasonable (but not conclusive) link between the sites (Wassersug-EPA, 2/5/85a). Additionally, the only way to strengthen this link would be the installation of a number of very expensive monitoring wells, the drilling of which could also cause environmental problems

(Wassersug-EPA, 2/5/85a). The approach would be to delist the site but to immediately relist it if further problems were encountered (Wassersug-EPA, 2/5/85a).

EPA was concerned that there was no national precedent for this action. At that time, the public (other than Hammermill) had shown little interest in the site, so EPA recommended finalizing the report (Shoener-EPA, 8/84), making it available for public comment, and holding a public meeting if needed (Wassersug-EPA, 2/5/85b).

EPA Headquarters agreed that the delisting of the site would present a unique policy and technical issues. EPA also stated that a deletion proposal would be considered based on the determination that a threat to public health and welfare, and to the environment was no longer present at the site based on investigations by EPA Region III and its contractors (Stanton-EPA, 6/28/85). The proposal should include (1) contact with the appropriate office of the Commonwealth of Pennsylvania, (2) discussion of these requirements and past response costs with Hammermill Paper Company, and (3) implementation by PADER, Region III, and Hammermill of an acceptable advisory and monitoring system for potential exposure of drillers to releases of hydrogen sulfide gases (Stanton-EPA, 6/28/85).

The status report (Shoener-EPA, 8/84) was finalized into the RI/FS document "Summary of Investigations and Recommendations for Further Action" (Shoener, 10/85) and submitted to PADER and Hammermill for comment.

### 3.60 Growth in Outside Interest in Presque Isle (May 1985-April 1986)

John Walker was contacted by a number of parties interested in the Beach No. 7 well and its possible relation to the Hammermill injection program. These parties included private contractors (Walker-PADER, 5/24/85), the National Resources Defense Counsel (Walker-PADER, 11/27/85), and the Chemical Manufacturers Association (Walker-12/24/85). PADER assigned a central point of contact within the Bureau of State

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Parks to coordinate with all media and other state and federal agency representatives (Solano and Bittle-PADER, 7/18/85).

During the following winter, the Amicus Journal (published by the National Resources Defense Council) featured an article that criticized the underground injection of hazardous wastes and made the Presque Isle site its centerpiece (Brown, 1986). Hammermill vigorously objected to the following blatant factual errors (and misstatements) contained in Brown's article:

1. Brown (1986) identified the Beach No. 7 well as an oil well.
2. Brown believed that it produced oil from the Bass Island Formation.
3. He confused the blowout of Hammermill well 1 in 1968 with the seepage at Beach No. 7.
4. Brown implied that PADER and EPA were unaware that the wastes had been injected into the Bass Island Formation until the late 1970s (when permits were clearly on file).
5. Brown said that there was evidence to suggest that the waste may have "[weaved] its way all the way under Lake Erie into Canada and Michigan" (Rogers-HML, 4/16/86), while Hammermill says there was no evidence to suggest this.

Hammermill noted that it was apparent that Mr. Brown had not obtained or read any of the technical reports prepared by Hammermill or EPA, and he had no evidence linking Hammermill to the site. Rogers (HML, 4/16/86) mentions that ABC television's "20/20" program contacted Hammermill, but ABC decided not to pursue the story after learning of these reports.

### 3.61 Hammermill Comments on RI/FS Recommendations (December 1985-January 1986)

During an interview with Hammermill officials, Versar was provided with a copy of their comments on the "Summary of Investigations and Recommendations for Further Action" (Shoener, 10/85). Hammermill felt that the RI/FS document ignored some major findings in previous technical documents. However, Hammermill noted that the document indicates that there is no conclusive connection between Hammermill's deep well disposal activities and the former seepage from the Beach No. 7 well on Presque Isle (D'Appolonia/IT-HML, 12/20/85). Hammermill generally agreed with the report's recommendations and felt they would constitute a responsible course of future action.

Hammermill noted the recommendation to notify local oil and gas drillers in the Erie area of sulfur-laden water in the Bass Island Formation and that drillers should be prepared to seal the well if a potential hazard is recognized. Hammermill suggested that the recommendation should be modified to include the Lockport Formation as well (D'Appolonia/IT-HML 12/20/85). Monitoring of oil and gas well drilling should consist only of visual inspection by the local PADER oil and gas inspector, particularly because previous attempts at other wells had failed to obtain unadulterated samples (D'Appolonia/IT-HML, 12/20/85). Hammermill agreed that no environmental or human health threat justified the additional expenditures to construct deep monitoring wells (D'Appolonia/IT-HML, 12/20/85).

Mr. Shoener of EPA contacted Hammermill to determine if it would be interested in being involved in monitoring gas well-drilling activity in the immediate area. Hammermill indicated that it did not feel that it had any legal right to intrude on private well drilling activities or on private property, or to act in any official capacity. Further, Hammermill had no plans to participate in any water sampling (Andrews-HML, 1/16/86).

3.62 <u>Reports of Hydrogen Sulfide Releases Near Erie (May-June 1986)</u>

EPA received complaints from the Mill Creek Township Supervisors' office concerning a well that vented a large cloud of hydrogen sulfide gas on May 31, 1986, and prompted "hundreds of complaints" to the local fire and police departments (Palokas, 6/6/86). Mr. Ken Young (who was previously involved in the Presque Isle case with the Bureau of Water Quality Management), PADER's regional oil and gas manager, was also contacted (Palokas, 6/9/86). Mr. Palokas noted that the gas was encountered at a depth of 1800 feet below the surface (Palokas, 6/6/86).

The 1800 depth for the gas discharge is extremely important. The Bass Island Formation is reported to be at a depth 1500-1750 feet in the Erie area depending on location and geologic structure (Walker-PADER, 8/15/83). This suggests that the source of this hydrogen sulfide release would not have been the Bass Island Formation. The exact location of this problem well was not given in the correspondence, but describes the site as being between two large commercial buildings (Palokas, 6/6/86).

PADER oil well index maps for the Eric North quadrangle indicate that the only wells in the manufacturing area of Millcreek Township that fit this description are located near the airport. In this area, the Bass Island Formation is approximately 1080 feet below sea level (Walker-PADER, 8/15/83) to 1100 feet below sea level (D'Appolonia/IT-HML, 3/83). The highest elevation in this area is 770 feet. Therefore, this release could have been from the Bass Island Formation. However, these wells are very near to the Renkis well, whose fluid has been characterized as being a natural brine, and this area is at the outer limits of or beyond the distance that Koederitz predicted the brine could move (see Shoener-EPA, 10/85).

3.63 PADER Comments on the EPA RI/FS Document (September 1986)

The "Summary of Investigations and Recommendations for Further Action" (Shoener-EPA, 10/85) was reviewed by Mr. Mark Gorman of the Division of Emergency and Remedial Response, Bureau of Waste Management, in the PADER Meadville office. PADER agreed that the costs and risks associated with drilling a monitoring well were not warranted at this time, and made the following recommendations:

1. The agency or agencies responsible for notifying drillers, for monitoring drilling activities, and for collecting information from drillers should be formalized.

2. The characteristics, assumptions, restrictions, applicability, and reliability of the NEMESIS model used by Koederitz should be discussed or included as an appendix to the document in its final form (these aspects of the NEMESIS computer model are included in Section 6.0 of this report).

3.64 <u>Record Compilation, Record of Decision, and Delisting Support (November 1986-April 1987)</u>

Versar Inc. was hired by EPA Region III to compile records and to provide litigation support in determining the involvement of the PRP, Hammermill Paper Company, and in determining the appropriate criteria for a delisting petition and record of decision. Versar was to visit the site, discuss the site with PADER officials, and obtain and review PADER project files for incorporation into EPA Region III files. Versar was able to arrange a meeting with Hammermill officials and their consultants to discuss the historical and technical aspects of the site. Versar was granted free access to review and duplicate all Hammermill files on the site, including internal correspondence. Much of the PADER information and all of the internal Hammermill files have not previously been included in EPA's files.

The Beach No. 7 well at the Presque Isle site appears to be in good condition. Versar did not note any odors, discolored sand, or evidence of stressed vegetation. The well is typical of many in the Erie area, and it is surrounded by a small 4-foot high wooden fence. The Bass Island Formation was plugged 5 years ago; fresh sand was brought in to cover the area, and the nearby parking lot was removed.

Versar discussed the current status of the Presque Isle site with PADER officials in the Meadville Office. Mr. Ken Young, Manager of the Meadville Bureau of Oil and Gas, stated that there had been no confirmed releases of hydrogen sulfide gas since the Beach No. 7 well was plugged in October 1982. He commented that the reports of foul-smelling odors during oil and gas well drilling in the area were probably the result of naturally occurring, sulfurous, aromatic hydrocarbons which are typically associated with natural gas.

Mr. Young also mentioned that there is a considerable logistical problem involved with confirming a hydrogen sulfide release. The Erie County Department of Health or an oil and gas inspector must call the Bureau of Oil and Gas office, which then must obtain the test equipment from PADER-CERCLA, which then must get the equipment to the oil and gas inspector at the well. The amount of time required was usually too great to allow for sampling. The former Erie oil and gas inspector, Mr. Harry Mackey, often required that the driller have mud available to immediately stem the flow of hydrogen sulfide-bearing gases or fluids as a safety precaution.

Versar discussed the possibility of having EPA Region III supply a hydrogen sulfide meter for the exclusive use of the Erie County oil and gas inspector. All parties agreed that a meter obtained on loan from EPA Region III would eliminate these logistical problems and allow PADER to discriminate between the actual releases of hydrogen sulfide and the usual natural gas odors. In response to PADER's comments on the RI/FS (Shoener-EPA, 10/85), it was agreed that EPA would draft the letter notifying local drillers, and that the local PADER oil and gas inspector was in the best position to monitor oil and gas drilling and to gather further information on any potential problems with the Bass Island Formation.

Mr. Young felt that because (1) state law requires drillers to give 24-hour notice before drilling begins, and (2) it was already the policy of the Meadville office to have the local oil and gas inspector present when the Bass Island Formation is penetrated, it would not be necessary to incorporate these provisions into the permitting process.

Mr. Gorman stated that PADER felt that monitoring future drilling with some sort of hydrogen sulfide testing equipment over the next 5-10 years would appropriately protect the interests of the surrounding population in the event that the site was delisted. Such data would be enough to recognize whether a problem developed to justify relisting the site.

During the visit with Hammermill's consultant on December 10, 1986, Versar obtained copies of the 204 well logs showing the occurrence of black water in the Bass Island strata that D'Appolonia had mentioned in its October 27, 1983, report. These logs are now contained in the EPA/Versar project files, and they will be delivered along with the PADER files. The locations of these wells are shown in Figure 2-2, and they will be discussed more fully in Section 4.0 of this report.

Versar visited with Mr. Chris Laughery at the Pennsylvania Geologic Survey and obtained pertinent information on the locations of oil and gas wells in Erie County, as well as a draft of an upcoming survey publication on brine types in Pennsylvania (Dresel and Rose, 1985).

Versar met with Mr. John Walker of the Bureau of Parks, Mineral Section, to discuss technical aspects of the previous investigations. Mr. Walker has not been directly involved in the more recent investigations, but he dismisses the D'Appolonia/IT criticisms of his original investigations. He is skeptical of modeling in general, and he still maintains that the injection wells at Hammermill are the source of both the pressure-drive and chemical constituents of the seep at Beach No. 7.

Versar obtained copies of all PADER files duplicated for EPA Region III during November 1983, and copies of the files from that time to the present.

## 4.0 GEOLOGICAL IMPLICATIONS OF LINEAMENTS AND "BLACK WATER" OCCURRENCES

A central focus of the investigations concerning the Presque Isle site has been whether the discharge from the Bass Island Formation and the resulting seep at Beach No. 7 consisted of a naturally occurring fluid or contained the spent pulping liquor injected between 1964 and 1971 by Hammermill Paper Company. PADER and D'Appolonia/IT have presented numerous arguments on both sides of this issue.

There have been very few arguments over the geologic units involved here. Both PADER and D'Appolonia/IT now agree that Hammermill injected into the Bass Island Strata (includes the overlying Bois Blanc Formation), and the source of the seep at the Beach No. 7 well was the Bass Island Formation. The controversy centers on whether the contaminants could have reached the Beach No. 7 well under enough pressure to cause the well to flow from about 1971, when the injection wells were plugged, until 1982, when the Beach No. 7 well was plugged.

This section is a discussion of the lineament analyses presented in the past investigations, and the geographical distribution of the Erie County oil and gas wells that have shown evidence of black water or hydrogen sulfide gas and their relation to LANDSAT lineaments. These studies and the conclusions that have been drawn from them are extremely important, because (1) both D'Appolonia/IT (HML, 3/83) and Walker (PADER, 8/15/83) have made classic errors in the application of lineament analyses, (2) the underlying geological implications of these lineaments have not been properly discussed, and (3) the role of fracturing is a central assumption of the Koederitz reservoir simulations, and may be associated with black water occurrences in the Bass Island Formation.

### 4.1 Summary and Conclusions

Lineaments are not always direct indicators of fracture, and their occurrence is determined largely by the scale of observation. Lineaments must be supported by other geologic evidence to establish them as representing fracture zones. Available geologic information indicates that certain lineaments can be related to thinning and fracturing of the Salina evaporites, collapse of the Bass Island Formation, and the presence and thickening of the overlying Oriskany sandstone (Overby and Pasini, 1970). The east-west lineament postulated as being the fracture responsible for moving the Hammermill spent pulping liquor to the Beach No. 7 well is supported by available geologic information.

Both D'Appolonia (HML, 3/83) and Walker (PADER, 8/15/83) make errors in interpreting this east-west lineament and other lineaments in the Erie area. Compared with the available literature on LANDSAT-scale lineaments, Walker's (PADER, 8/15/83) interpretation is far too narrow, and D'Appolonia's (HML, 3/83) interpretation is far too broad. Neither a direct fracture connection nor a broad, diffuse, and homogeneous zone of fracturing is supported by the available literature.

Black water has been reported in the Bass Island Formation at about 8 percent of the deep wells in the northern 16 quadrangles in Erie County. Of these 204 wells, 9 percent (i.e., 19 wells) were drilled by companies other than Envirogas. This calls into question the idea that these well logs are in error, unless nine other companies also made the same error. There is a geographical relationship between these black water occurrences, the presence of the Oriskany sandstone, and lineaments in the Erie area. The occurrence of black water, either introduced by older drilling or as a natural phenomenon, suggests that black water in the Bass Island Formation should be considered a background condition in comparing data from Presque Isle's Beach No. 7 well.

## 4.2 Nature of LANDSAT Lineaments

Perhaps the most important concept to introduce at the outset is this. While many fracture traces are lineaments, not all lineaments are fractures. A lineament is any linear feature observed through areal photography. This may include ridges, valleys, streams, and other geomorphic features, as well as roads, fencelines, agricultural areas, and other man-made features. Glacial striations are other obvious lineations in the area of Erie County Pennsylvania. In oblique areal photography, the angle at which the photographs are taken is important. In LANDSAT imagery, the computer enhancement can introduce errors to the observer. Wise (1982) presents an excellent brief, tongue-in-cheek, discussion of common errors in lineament analyses.

Lattman (1958) introduced the term "fracture trace" to describe short linear features less than a mile long and suggested that they are traces of joints or small faults. Joints are fractures that show no displacement whereas faults are fractures that have displacement (i.e., the rock on one side of the fracture is offset from the rock on the other side). The term "fracture trace" is misleading because it implies a genetic origin of the feature. A short lineament may not be related to faulting or jointing; additional geologic evidence should be obtained to verify the role of fracturing before attributing the occurrence of a "fracture trace" to larger fracture zones.

The number of lineaments observed in any given study is largely determined by the scale of the investigation. Koederitz (EPA, 5/23/83) notes that the most recent lineament study (Figure 4-1) did not show the east-west lineaments identified in the earlier investigations (Figure 3-7). The reason is that the level of observation is governed, for the most part, by the scale of the map and the areal photographs employed by the investigator. Figure 3-7 is based on an examination of 7.5-minute quadrangles at a scale of 1:24,000; Figure 4-1 is based on standard 1:250,000 LANDSAT imagery. Correspondingly, Figure 3-12 from D'Appolonia (HML, 3/83) is based on enlarged LANDSAT imagery. Therefore it shows more lineaments than does Figure 4-1, but fewer lineaments than Figure 3-7. Notably, the D'Appolonia (HML, 3/83) map (Figure 3-12) shows the same east-west lineament of Figure 3-7 from Walker (PADER, 8/15/83) which passes through both the Hammermill facility and the Beach No. 7 well.

FIGURE 4-1
LANDSAT LINEAMENT ANALYSIS
(EPA REGION III FILE UNDATED)

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## 4.3 Relation of Lineaments to Geologic Structure in Erie County

Overby and Pasini (1970) studied lineaments in the Springfield Township of western Erie County (Figure 4-2). North-northeast, northwest, and east-northeast trending lineaments can be related to localized thinning of the Salina Formation caused by dissolution of evaporates from flow through fractures, the collapse of the Bass Island Formation, and the occurrence of natural gas in the Oriskany sandstone (Figure 4-2). The dissolution of Salina evaporates must have occurred during the deposition of the Oriskany sandstone, which thickens over these zones (Figure 4-2), and before the deposition of the overlying Onandoga Formation, which is unaffected (Overby and Pasini, 1970).

Using the concepts of Overby and Pasini (1970) developed for Springfield Township, Versar overlayed the lineament analysis of D'Appolonia (HML, 3/83) onto the known subsurface outcrop pattern of the Oriskany Formation shown in Pennsylvania Geologic Survey Bulletin G27. There is good agreement between the distribution of the Oriskany Formation and the geographic locations of northwest, northeast, north, and east-west trending lineaments (Figure 4-3). These relationships suggest that the east-west trending lineament running between the Hammermill facility and the Beach No. 7 well may be the expression of a fracture zone in the subsurface which affects the Bass Island Formation. Other Lineaments (shown prominently on the 1:250,000 LANDSAT inquiry) correspond with glacial striations in the Erie County topography.

## 4.4 Interpretations by Walker (PADER, 8/15/83) and D'Appolonia (3/83)

Several LANDSAT-scale lineaments in the Appalachian Plateau Province (the geologic setting of Erie, Pennsylvania) have been the subject of intensive field study and can serve as guidance in interpreting the lineaments discussed by Walker (PADER, 8/15/83) and D'Appolonia (HML, 3/83). These lineaments are the Petersburg and Parsons lineaments of West Virginia (Wheeler, 1980 ;Wilson, 1980), and the Tyrone-Mt. Union cross-strike lineament of western Pennsylvania (Rogers and Anderson, 1984). These lineaments are typically localized zones (a few miles or so

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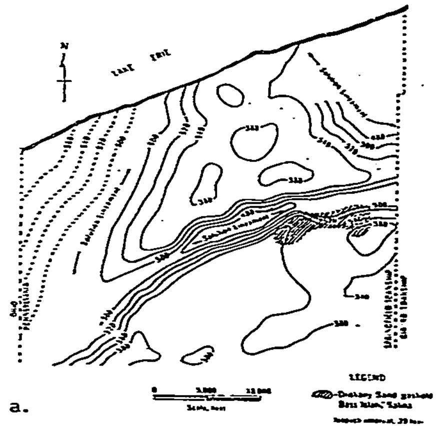
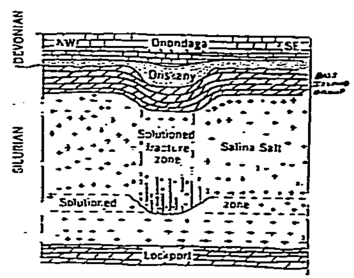
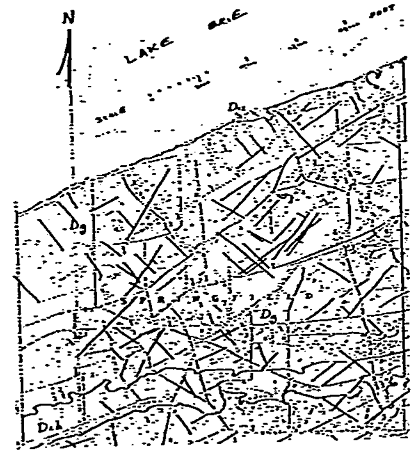



a.




b.




c.

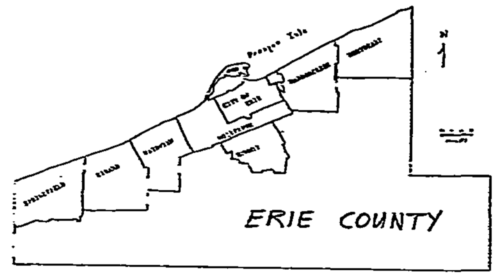



FIGURE 4-2
ISOPACH MAP OF BASS-ISLAND SALINA GROUP SHOWING SOLUTION LINEAMENTS AND ORISKANY GAS FIELD (a), CROSS SECTION SHOWING SOLUTIONED FRACTURE ZONE AND THICKENING OF ORISKANY SANDSTONE (b), AND LINEAMENT ANALYSIS FOR SPRINGFIELD TOWNSHIP, ERIE COUNTY, PENNSYLVANIA (c)
(Richards et. al, 1985 )

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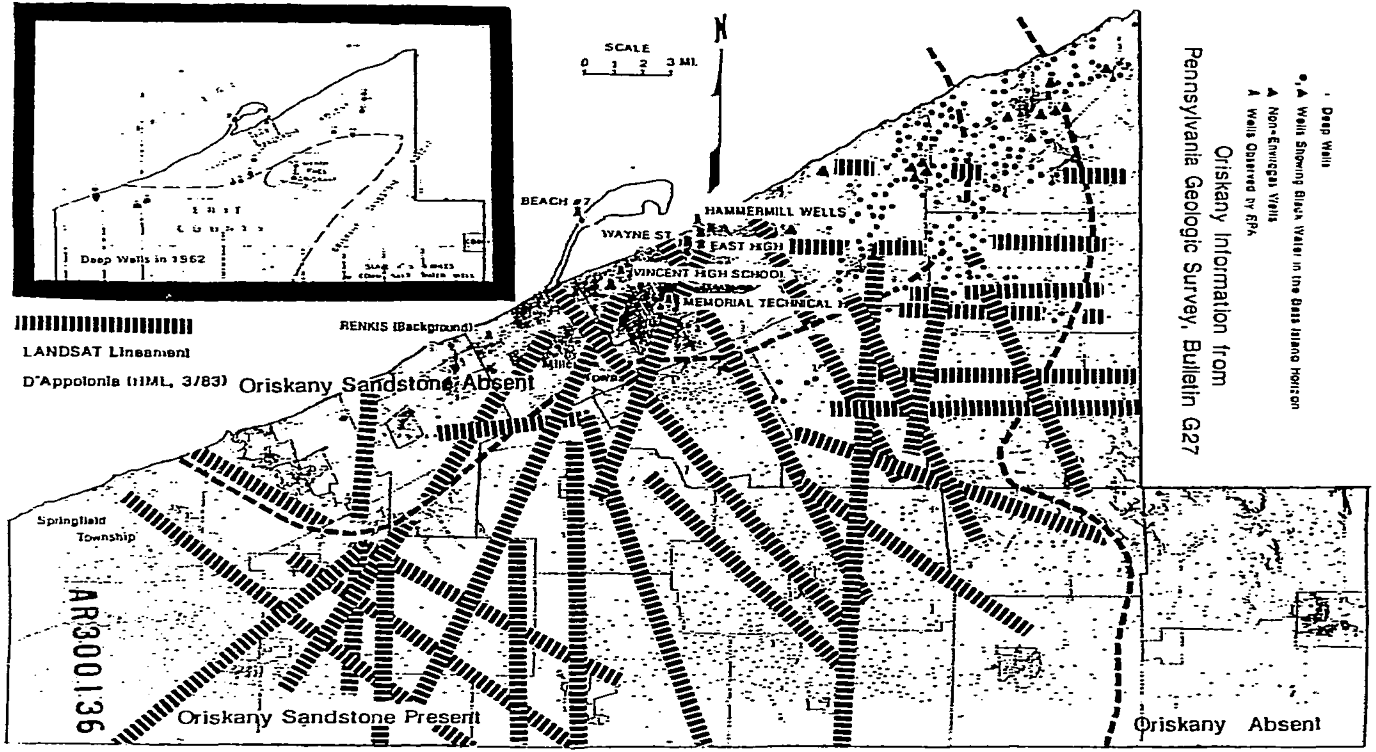


FIGURE 4-3
BLACK WATER, RELATION TO ORISKANY AND LINEAMENTS

wide) of statistically significant increases in jointing caused by differential subsidence of deep crustal blocks or lateral movement of thrust sheets. As such, they are rarely interpreted as either discrete single fractures or as indicative of homogeneous, regional fracture patterns.

D'Appolonia (HML, 3/83) attempts to use the large number of lineaments in the Erie area as a basis for supporting the radial flow assumptions of its GEOFLOW reservoir simulation. This assumption is not altogether unreasonable, but it fails to consider the best available information in the literature on the nature of lineaments and fractures. Walker (PADER, 8/15/83) points out that these lineaments are spaced approximately 2 miles apart (Figure 4-3). In this sense, Walker (PADER, 8/15/83) is correct but for the wrong reasons. The literature supports mile-wide zones of intense fracturing (Overy and Pasini, 1970) (see Figure 4-1). Therefore, D'Appolonia (HML, 3/83) is interpreting the relation of lineaments to fractures too broadly. On the other hand, Walker's (PADER, 8/15/83) interpretations are far narrower than the literature will support.

The central focus of Walker's (PADER, 8/15/83) hypothesis is that a discrete fracture zone extends from the Hammermill injection wells to the the Beach No. 7 well, and the zone allows both the pulping liquor and the rapid pressure build-up to reach Presque Isle, causing the seepage of hydrogen sulfide-bearing fluids to the surface. Pore-plugging reactions must immediately ensue following the end of the injection program in order to maintain this pressure drive from the early 1970s to 1982. When Walker (PADER, 8/15/83) employed the Hagen-Poisuelle equation for flow in a cylindrical pipe, he noted that a pore space diameter of only 0.5 centimeters is sufficient to cause the flow at the Beach No. 7 well. In other discussions (McCoy-USGS, 12/3/82), Walker suggests that the injection fluid could have moved over 70 miles to near Niagara Falls, New York, if a fracture system could provide a conduit only 5 inches in diameter.

Employing a pipe analogy is not a bad first approximation of flow in a fracture. The equation that Walker (PADER, 8/15/83) uses is appropriate for laminar flow. Walker (PADER, 8/15/83) takes the observed pressure at the Beach No. 7 well, and other reasonable assumptions of reservoir properties, and solves for the minimum pipe (or in this analogy, the pore space) diameter; this concept is misleading. The best available literature suggests that a LANDSAT lineament encompasses an area of intense fracturing a mile or so wide, the porous zone of the Bass Island Formation is considered to be 20 feet thick, and the effective porosity is assumed to be 11 percent. These parameters would indicate that the "pore space diameter" (to use Walker's term) could be on the order of 185 feet in diameter (11,616 square feet).

The injection pressure would be dissipated over a large area. The question should not be how small a diameter is needed, but how large. It is conceptually obvious that pressure could be built up in an opening with a very small diameter. The important matter is not whether the pressure buildup could occur through a soda straw, but whether it could be built up in a tunnel the size of a cavern. This analogy does not even consider the friction imposed by the intervening matrix and the resultant turbulent flow.

### 4.5 Black Water Occurrences in the Bass Island Formation

Versar obtained 204 well logs from Hammermill's consultant, D'Appolonia/IT, that note the occurrence of black water in the Bass Island Formation, in its stratigraphic equivalents, or in the overlying formation (Akron dolomite, Camillus shale, or Onandoga limestone). Of the 204 well logs, 19 were drilled by other companies besides Envirogas. Versar located 2505 deep wells in the 16 quadrangles in the northern section (most of) Erie County, Pennsylvania. Therefore, roughly 8 percent of all deep wells report black water in the Bass Island Strata, horizon, and among these, 9 percent were drilled by companies other than Envirogas.

Kevin Carrol of Envirogas was correct in saying that the Bass Island Formation is characterized by a clear brine. This is true in 92 percent of the cases. However, this does not necessarily mean that the the 8 percent are spurious; that would necessitate that Carrol did not notice the mistake by his drillers during over 3 years of drilling or he did not correct it, and that nine other companies also made the same mistake.

The geographic distribution of the non-Envirogas wells covers about the same area as the Envirogas wells (Figure 2-2, and Figure 4-3). Additionally, the non-Envirogas wells appear to be closely associated with the same geologic feature thought to control the distribution of black water within the Bass Island Formation.

### 4.6 Relation Between Black Water, the Oriskany Sandstone and Lineaments

As noted by Overby and Pasini (1970), there appears to be a genetic relationship between some lineaments, fracture zones and the dissolution of the Salina evaporites, collapse of the Bass Island Formation, and the thickening of the Oriskany Formation. D'Appolonia (HML, 3/83) notes that the Oriskany sandstone in the Summit gas storage field (see Figure 3-13) has "sour gas," or a sulfurous odor problem, and that Van Tyne Consultants of New York has stated that black water in the Bass Island Formation is related to the presence of the Oriskany Formation. Mr. Arthur Van Tyne, president of this company, informed Versar that fractures also localize the occurrence of black water in the Bass Island Formation (personal communication, 2/10/87).

The geographic distribution of black water occurrences supports these concepts. The largest concentrations of black water are near the narrow tongue of Oriskany Sandstone in the Orchard Beach, Burgess, and Huornoy fields, or they are related to the prominent north and north-northwest trending lineaments passing through the Harborcreek and Huornoy fields (compare Figure 3-13 with Figure 4-3). Additionally, there is a strong relationship between the black water occurrences and the east-west trending lineaments (Figure 4-3).

## 4.7 Pre-injection Black Water Occurrences

Only two of the known black water occurrences predate the Hammermill injection program: the the Hoard/Lewis Parker No. 1 well drilled in 1914, and the Thompson No. 1 well drilled in 1960. Both wells are located in the Northeast field (see Figure 3-13). The remaining 202 wells were drilled between 1977 and 1980. Walker (PADER, 8/15/83) has ascribed the occurrence of black water in the 1914 and 1960 wells to cross-contamination from the Lockport Formation, which is know to contain a naturally occurring black water. Walker attributes any post-injection occurrences to driller error, or he suggests that the occurrence is the result of Hammermill's injection liquor being present. Clearly, Walker (PADER, 8/15/83) is trying to have it both ways.

The increase in reports of black water during the 1970s should not be simply attributed to the Hammermill pulping waste based on the years it was discovered during well drilling. Most of the deep drilling that took place in Erie County occurred during the late 1970s, after the Hammermill injection program had ceased. Of the 53 deep oil and gas fields in Erie County, 41 of them were discovered after the Hammermill injection program ended.

Walker (PADER, 8/15/83) is quite critical of the Dow feasibility study (HML, 11/19/62), because he claims it did not consider all the possibilities of where the waste might have migrated, and that underground injection programs should not be sited in areas where there are large numbers of oil and gas wells. However, an examination of Pennsylvania (1960) well maps and the Dow (HML, 11/19/62) feasibility study (see inset, Figure 4-3) would indicate that there were very few wells in the Erie area when Hammermill began its injection program.

## 4.8 Implications for Background Comparisons

Walker (PADER, 8/15/83) suggests that the 1914 and 1960 wells were cross-contaminated by Lockport Formation fluids as the result of older drilling activities. The above discussion suggests that black water occurrences, although somewhat localized, may be natural. Even if Walker's (PADER, 8/15/83) arguments are accepted as the only reliable explanation, then black water in the Bass Island Formation is a reasonable standard for background comparison. In surficial soil sampling at other NPL sites, the contributions of lead and other contaminants from auto exhaust or other man-made sources at offsite locations are routinely considered.

The whole concept of background sampling is an attempt to measure the impact of human agents on the area as a whole, compared with the concentration at the site in question. Conceptually, there is little difference in this situation. Dr. Koederitz, reservoir simulations indicate that the injected fluid could not have migrated more than 6-7 miles. If areas beyond this distance show contamination of the Bass Island Formation with Lockport Formation fluids as a result of routine activities of man, then this fluid composition should also be considered as indicative of background conditions when evaluating chemical data from the Beach No. 7 well. If the Bass Island Formation naturally contains a black water, as some evidence indicates, this is even more important.

## 5.0 CHEMISTRY/GEOCHEMISTRY

### 5.1 Summary and Conclusions

The primary objective of the chemistry/geochemistry evaluation was to determine the origin of the seep fluids and the influence of the Hammermill pulping liquor at the Presque Isle site.

The seep fluid at the Presque Isle well (noted as "the Beach No. 7 well in some previous investigations) probably consists of Bass Island brine that has undergone chemical reactions after leaving the original geological formation. Based on the available data, no conclusive evidence can be formulated to support or deny the presence of pulping liquor in the seep fluids or in the Bass Island brines at the Presque Isle site. If pulping liquor is present at the Presque Isle location, it probably has been diluted at least 10- to 20-fold with brine, possibly on the order of 100- to 1,000-fold.

Additional monitoring would be necessary to resolve ambiguities. The analytical design of any proposed program should bear in mind the weaknesses and faults noted in these past investigations. There are many techniques, such as the carbon preference index (CPI) and stable isotope ratios, that are appealing. Any methods that might be utilized should be evaluated for their accuracy, precision, and interactions with the background chemistry, especially in light of the substantial dilutions that may have occurred.

The subsurface zone that received the injected wastes may include the Bass Island Formation and the Bois Blanc Formation. In this section, we do not distinguish between the two formations; thus the term "Bass Island Formation" refers to the entire subsurface zone that received injected wastes.

An evaluation of the analytical information resulted in the following conclusions:

Major Ions

- The Lockport and the Bass Island brines at Presque Isle are comparable to regional subsurface brines (with the possible exception of boron).
- There are distinctive differences between brines from the Lockport and Bass Island formations at Presque Isle.
- The seep at Presque Isle probably originated from the Bass Island brine at Presque Isle.
- Local variations in the major ion chemistry suggest a significant amount of natural brine heterogeneity.
- Based on the major ion chemistry variability, any pulping liquor that may be present in the brines would make up less than 5-10 percent of the total brine.

Field and Physical Measurements

- Conductivity and pH data should only be used to support other evidence, because they do not reveal conclusive information.
- The specific gravity and the filterable residue data suggest that the Bass Island brine is the source fluid for the seep.
- The results of the nonfilterable residue analyses could be explained by reactions occurring after the injection of pulping waste into subsurface formations.
- There is no evidence to confirm the occurrence of post-injection reactions due in part to the lack of available sample analyses. Enroute filtration and dilution ratios of the brine greater than 100-fold could conceal elevated levels of particulates that might form as the result of such reactions.
- Relatively low redox measurements indicate mild to moderate reducing environments in the formations. Under these conditions, variable levels of hydrogen sulfide and reduced iron are probably present. Analyses of these and related compounds may be suspect due to the critical nature of proper sampling and analysis techniques.

Inorganics (not including metals)

- The lack of available data for comparative purposes severely limits the evaluation. The results of many analyses demonstrate large variability.

- The acidity data supports the theory that the Bass Island brine at Presque Isle serves as the origin of the seep.

- Alkalinity and acidity results suggest that the Neutracel I solution may not be a plausible duplicate for the original injection liquor.

- If surfactants act in a conservative manner, any pulping liquor present at the Presque Isle site must have been diluted 3- to 36-fold. This conclusion may be moot if comparative data on natural brines show any significant levels of surfactants.

- The data suggest diagenetic reactions may have taken place at Presque Isle. Due to a lack of comparative information, no conclusion can be reached regarding the possible presence of pulping liquor at the site.

- A hypothesis involving pulping liquor at Presque Isle would account for sulfide results. Further evaluation of the theory suffers from the lack of available quantitative data.

Metals

- A large amount of variability in the results, coupled with low sample concentrations, precluded any conclusions, except with regard to the lithium data.

- Lithium concentrations suggested a connection between the seep and the Bass Island brines at Presque Isle.

Volatile Organic Compounds

- Due in part to inconsistencies in detection limits and significant interlaboratory variation, the volatile organic information cannot be used to support or deny the existence of the liquor at the Presque Isle site.

Semivolatile and Tentatively Identified Compound (TIC) Groups

- Significant interlaboratory variation, detection limit uncertainties, and the lack of comparable quantitative data result in a database that yields no conclusive information.

- Analyses of phenol may represent a 621:1 dilution of the pulping liquor with brine at the East High School Well. Phenol may be useful in monitoring the presence of the pulping liquor in other areas, since there was no significant background in the subsurface brine samples.

Target Compounds

- The results for the first 18 target compounds (Table 5-7) are not very useful in this evaluation. The available data cannot be used to decisively indicate the absence or presence of pulping waste at the Presque Isle site.

- The available data on acetate and formate suggest that there are no pulping wastes at the Presque Isle site. However, there are two problems in confirming the suggestion. The first is the absence of analyses at the background Renkis Well. The second involves potential degradation processes that could account for remnants of the pulping wastes at the site.

- The tannin-lignin (T-L) results may be strongly affected by sampling and analytical problems. If the T-L measurement represents conservative behavior, the pulping waste exhibited a 270:1 dilution with brine at the East High School Well. Due to large laboratory variation, the T-L results suggest either high background levels or pulping waste contamination in the Bass Island formation at the Presque Isle and Renkis sites.

- The "low-level" lignin analyses provided by Cooper-Driver and Wilson (EPA, 7/4/84) result in a dual explanation of the data. Since no significant amounts of lignin were observed at the sites, either (1) no pulping wastes were present, or (2) if present, a large dilution occurred, or (3) if present, lignin was removed from the waste en route to the site.

- The available results of direct analyses for the microbicide, Busan 881, and its components do not provide any useful comparative information for this investigation.

- The results of GC "fingerprint" analyses did not prove a connection between contaminated brine at the East High School Well and the Bass Island brine at the Presque Isle site. However, due to the unknown origin of the qualitative fingerprint, the results cannot be used to disprove the presence of the pulping liquor at the Presque Isle site.

The chemical evaluation of the samples is presented in the following subsections by constituent groups. There are cases in which some elements are not found in their typical analytical groups (i.e., most of the major ions are best analytically described as metals). However, the advantages of comparing samples by a constituent group outweighs the conceptual difficulties. Initially, the concentrations of major ions

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found in subsurface brines will be compared to the levels in the various samples to determine the principal origin of the various fluids. After this first evaluation, the results of field and physical measurements will be examined, followed by the assessment of less concentrated constituent groups, such as general inorganics, metals, and pollutant organics. Subsequent to these comparisons, the results of "target" compounds (possibly related to pulping wastes) will be evaluated.

A substantial amount of chemical data have been generated during the environmental investigation of the Presque Isle site. In many cases, detailed information about the sampling and analysis methods was not available or was incomplete. Specific critiques of reports are not included here unless they are thought to influence the evaluation of the samples. The summary tables (5-1 to 5-7) are designed to consolidate the available chemical information. This method of presentation has been also chosen in order to lessen ambiguities resulting from interlaboratory variation and inconsistencies in the sampling techniques. The consolidation accomplishes this objective at the possible sacrifice of specific data of interest. Data that are thought to be suspect or indicative of special conditions are footnoted. The data for dissolved and total fractions are separated only when significant variations occurred or were important to the evaluation.

### 5.2 Major Ions

The tabulated summary of major ion concentrations from available sample data can be found in Table 5-1. This consolidation represents laboratory data from PADER, USGS, EPA, Weston, Hammermill, D'Appolonia/IT, Dow, Poth, and Dresel and Rose. The data were obtained from the references noted in the summary table.

Samples taken of the seep during 1979 were not extensively analyzed. Of the major ions, only the boron and chloride in these samples were analyzed. These values can be compared to the more complete results from 1982 seep samples. The chloride concentrations of the

TABLE 5-1
RESULTS OF MAJOR IONS ANALYSES

| Parameter | Units | Presque Isle Well: Seep 1979[a] | Presque Isle Well: Seep 1982[b] | Presque Isle Well: Lockport Form. 1982[b] | Presque Isle Well: Bass Is. Form. 1979–1981[a] | Presque Isle Well: Bass Is. Form. 1982[b] |
|---|---|---|---|---|---|---|
| Barium | mg/l | NA | <1–12.2[c] | <1–7.75[a] | <1–12 | <1–10[d] |
| Boron | mg/l | 400–470 | 150–180 | 44[b]–75[f] | (63–400)[e] | 160 |
| Calcium | g/l | NA | 36–40 | 13.7–16.5 | 35–43 | 36–37 |
| Chloride | g/l | 186–195 | 175–184 | 132–136 | (114–232)[e] | 175–186 |
| Magnesium | g/l | NA | 9.35–10.9 | 3.20–3.35 | 8.8–10.7 | 8.5–10.1 |
| Potassium | g/l | NA | 3.7–4.4 | 1.2–1.5 | 5.8 | 3.8–4.7 |
| Sodium | g/l | NA | 48–56 | 60.5–64 | 49.3–52.9 | 47–65 |
| Strontium | g/l | NA | 1.35–2.09[f] | 0.122–.344 | 2.2–2.5 | 0.9–1.43 |

| Parameter | Units | Renkis Well: Bass Is. Form 1982[b] | Hammermill #1: Bass Is. Form. Pre-1964[a] | Other Wells: Oriskany Form. 1962[g] | West Penn.: Brines 1962[g] | Oilfield Brines: Oriskany Form. 1985[h] |
|---|---|---|---|---|---|---|
| Barium | mg/l | 5.5[b]–16[f] | NA | NA | 2–1080 | 1.51–4.37 |
| Boron | mg/l | 97 | NA | NA | ND–0.8 | NA |
| Calcium | g/l | 41 | 33.8 | 37.3 | 0.032–38.4 | 8.93–28.4 |
| Chloride | g/l | 180–190 | 147 | 161 | 2.81–170 | 58.9–207 |
| Magnesium | g/l | 10 | 7.88 | 8.28 | 0.0089–8.28 | 0.797–2.39 |
| Potassium | g/l | 4.5 | 3.67 | 3.97 | 0.012–3.97 | 0.978–3.89 |
| Sodium | g/l | 51–121[i] | 39.5 | 42.8 | 1.98–66.1 | 24.4–83.3 |
| Strontium | g/l | 1.25–2.3 | NA | NA | ND–0.321 | 4.4–13.1 |

(Continued)

TABLE 5-1
RESULTS OF MAJOR IONS ANALYSES
(Continued)

| Parameter | Units | Hammermill Injection Liquor 1962[j] | Neutracel I Pulping Liquor 1983[k] | East H.S. Well Bass Is. Form. 1984[l] |
|---|---|---|---|---|
| Barium | mg/l | NA | 0.0028 | NA |
| Boron | mg/l | NA | 0.0009 | 105-130 |
| Calcium | g/l | 0.032 | 0.082 | 41-42 |
| Chloride | g/l | 0.27 | 5.3[m] | 190-193 |
| Magnesium | g/l | 0.024 | 0.053 | 9.7-10 |
| Potassium | g/l | NA | 0.280 | 4.3-4.5 |
| Sodium | g/l | NA | 14 | 47-50 |
| Strontium | g/l | NA | 0.0013 | 0.220-1.2 |

Range of values are noted when multiple samplings and analyses were available. The ranges are inclusive of total dissolved analyses when available. Significant deviations between the components are footnoted.

Acronyms and Abbreviations:

NA = Not Available.

ND = Not Detected. Detection limit was not available.

D = Dissolved

T = Total

[a]From attachments to *Ecology and Environment, Inc.* (1982).

[b]*From* D'Appolonia/IT (1983).

[c]Value *represents* the total analysis and is considered suspect. All other results (both dissolved and total) are less than 1 mg/l.

[d]Significant variations in interlaboratory results (both total and dissolved).

[e]Large range of values over different sampling events and laboratories were *utilized*.

[f]Value represents the total analysis and may be suspect. Other "total" results are approximately 1.45 g Sr/l.

[g]Originally Poth (1962). Ranges taken *from* D'Appolonia/IT *Interim* Report, August 15, 1983.

[h]From Dresel and Rose (1985). *Data only from* Oriskany Formation.

[i]Value is the total analysis by PADER *and* may be suspect. Other brine samples have approximately half of this value.

[j]*From* Dow Industrial Service, (1962).

[k]Pulping liquor produced on a laboratory scale and analyzed by IT Corporation and Battelle. From D'Appolonia/IT (1984)

[l]From D'Appolonia/IT (1985). Values were consolidated from USGS and IT laboratory analyses.

[m]Represents the initial analysis. A re-analysis gave a value of 0.05 g Cl/l, which may be suspect *due to the* presence of large amounts of cations and total dissolved solids.

latter samples were essentially the same level as samples analyzed in 1979. However, the 1979 boron levels of 400-470 milligrams per liter (mg/l) dramatically dropped to 150-180 mg/l during the 1982 sampling of the seep. The accuracy of the boron analyses during the two sampling periods cannot be evaluated at this time, and the analytical results will be considered to be representative for the sampling periods.

Analyses of the brine from the Bass Island formation at Presque Isle were comparable for most of the major ions during the 1979-1981 and 1982 sampling periods. Boron concentrations during the period 1979-1981 were variable (63-400 mg/l) but exhibited a general decreasing trend (this was apparent in the complete PADER data summary, Ecology and Environment, 1982). The boron level (160 mg/l) during 1982 was encompassed in the analytical range of the data from the earlier period. The significance of this decrease in boron concentrations of the seep and Bass Island samples at Presque Isle is not apparent at this time.

A comparison of the brine chemistry from the Lockport and Bass Island formations at Presque Isle reveals distinctive differences. Concentrations of boron, calcium, chloride, magnesium, potassium, and strontium in the samples from the Lockport Formation are significantly lower than those from the Bass Island Formation. Sodium and barium analyses of samples from the formations yielded variable results that were not distinctly different. In general, the major ions provide a definite signature that can be used to help trace the origin of related fluids.

The brines sampled at Presque Isle should also be evaluated relative to subsurface brines from both nearby and regional wells. Poth (1962) analyzed brines from western Pennsylvania, several of which were from the Oriskany Formation. The Oriskany Formation occupies a similar regional stratigraphic position as the Bass Island Formation (closely associated with the Salina evaporites) but thins out in the area of Presque Isle. Because of limited chemical data on the Bass Island brines, information on subsurface brines (the Oriskany Formation brines in particular) can be used in a general evaluation. More extensive chemical information on brines from the Oriskany can also be found in Dresel and Rose (1985).

The major-ion concentrations of the Lockport and Bass Island brines at Presque Isle are similar to those reported for regional brines, but there are some notable exceptions. Boron levels in the Lockport and Bass Island brines at Presque Isle (44-160 mg/l) are definitely higher than any reported for regional brines but they may be an artifact of different analytical procedures. Based on the information currently available, this problem cannot be further evaluated at this time. With the exception of boron, the levels of major ions in Lockport brine at Presque Isle fall within the range of values for the regional brines. Bass Island brines at Presque Isle demonstrate slightly elevated levels of magnesium and potassium relative to regional brines. These magnesium and potassium anomalies may be indicative of local heterogeneities in the Bass Island Formation. The Bass Island brine at Presque Isle contains a peculiar amount of strontium (0.9-2.5 g/l). This concentration is above the values (max. = 0.321 g Sr/l) reported by Poth (1962) for western Pennsylvania brines and below those measured by Dresel and Rose (1985) for oilfield brines (4.4-13.1 g Sr/l) from the Oriskany Formation.

In order to address the question of contaminants occurring at the Presque Isle site, a distinction has to be made between natural heterogeneities and variations in natural fluids due to injected wastes or other natural fluids. An examination of the chemical results of brine samples taken closer to the Presque Isle site can help to discern these differences.

For three nearby locations, analytical data on the brines were available. The Renkis well is located 5.5 miles southwest of Presque Isle and is considered to be a background or control for Bass Island brine. The samples from the Renkis well are comparable to the Bass Island brines at Presque Isle for most of the major ions. Boron was lower and strontium was slightly higher at the Renkis well relative to the 1982 analyses of the Bass Island brine from Presque Isle. The results of previous analyses (1979-1981) of the Bass Island brine at Presque Isle included ranges of boron and strontium that would overlap with those found at the Renkis well in 1982. Thus, no conclusive distinctions can be made between the Bass Island brines at the two sites. Analyses of the brine from Hammermill #1 (assumed to be from the Bass Island Formation) prior to the injection program (Dow-HML, 11/19/62) did not show any appreciable differences from 1979-1982 analyses of the Bass Island brine at Presque Island. The same is true of the 1984 major-ion analyses of the Bass Island brine from the East High School well.

The lack of significant differences in the major ions between the Bass Island brines at Presque Isle and the East High School site is very important. The brines at the East High School site are considered to be contaminated by pulping liquors but do not show deviations in the major ions. For a deviation to be apparent, the effect of the injected fluid (natural or "human-altered") has to exceed the analytical uncertainty and natural variability. The major ion concentrations in the 1962 Hammermill Injection Liquor and the 1983 Neutracel I Pulping Liquor are very low. Any presence of these fluids in a brine would serve only to dilute the major ions in the brine.

An analytical uncertainty of ±5 percent (a reasonable assumption) would mean that the pulping liquor would have to compose 5 percent of a contaminated brine before the analytical method could begin to measure the dilution. The reciprocal of the argument is that the pulping liquor could only be diluted 20X before its analytical signal for major ions would be lost in the background. The inclusion of natural variability (estimated ±10 percent for the major ions) in the discussion would result in the calculation of only a 10-fold dilution before the contaminant signal is lost.

The discussion above is based on the assumption that the major ions are acting conservatively. While practically all of the major ions in brines could be involved in in situ reactions between the brine solution and evaporite mineral phases, there is no evidence from the data to support this hypothesis.

There is evidence, however, to suggest that the seep at Presque Isle did originate from the Bass Island Formation. The major ion concentrations in the 1982 samples of the seep and the Bass Island Formation are virtually identical.

## 5.3 Field and Physical Measurements

The available sample data of the field and physical measurements are summarized in Table 5-2. The information represents data from PADER, USGS, EPA, D'Appolonia/IT, Dow, and Dresel and Rose. The data were obtained from the references noted in the summary.

The results of these recent measurements are not very useful in this investigation. The pH measurements of the samples (pH 5.2-6.6) can be significantly altered by sampling artifacts. Dresel and Rose (1985) demonstrated that brines undergo chemical alteration that can begin immediately after the sample is obtained. They noticed pH differences (up to several pH units) between samples measured in the field and after storage. Dresel and Rose (1985) also discussed how factors such as temperature variations, changes in liquid junction potentials, and bromide poisoning can limit the accuracy of field measurements to $\pm 0.2$ pH units. They also referenced and supported the work of Kharaka et al. (1983) who noted that the loss of $CO_2$ from samples could increase the pH values. The relatively narrow range of pH measured between the samples cannot be used conclusively to point out any significant differences between the fluids.

The interpretation of the specific conductance data is somewhat confusing in light of previous chemical evidence. The conductance of the seep (400-575 mmhos/cm) is higher than that of brines (300-400 mmhos/cm)

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TABLE 5-2
RESULTS OF FIELD AND PHYSICAL MEASUREMENTS

| | | Presque Isle Well | | | | |
|---|---|---|---|---|---|---|
| Parameter | Units | Seep 1979–1981[a] | Seep 1982[b] | Lockport Form. 1982[b] | Bass Is. Form. 1979–1981[a] | Bass Is. Form. 1982[b] |
| Temperature (field) | °C | NA | 13–23 | 22 | NA | 20–20.5 |
| pH: | | | | | | |
| Field | pH units | NA | 5.55–5.85 | NA–5.60 | 5.6–5.6 | NA–6.60 |
| Laboratory | pH units | 5.9–6.4 | 5.50–6.00 | 5.8–6.2 | 5.2?–6.3? | 2.7[c]–6.4 |
| Eh (field) | mV | NA | (–78)–(–10) | (–34) | NA | (+110) |
| Oxygen (dissolved) | mg/l | NA | NA | NA | NA | NA |
| Specific Conductance: | | | | | | |
| Field | mmhos/cm @25°C | 188? | 412–575 | 300 | 140?–625? | 310 |
| Laboratory | mmhos/cm @25°C | NA | 400–432 | 343 | 216 | >100–400 |
| Specific Gravity | | NA | 1.182–1.200 | 1.136–1.152 | NA | 1.186–1.200 |
| Color: | | | | | | |
| Apparent | APHA Units | 300? | >500 | >500 | 5–15? | >500 |
| True | APHA Units | NA | 10–54 | 20 | NA | 76 |
| Residue: | | | | | | |
| Filterable (TDS) | g/l | 325? | 269–295 | 208 | 278?–408? | 266 |
| Nonfilterable (TSS) | g/l | 1.22? | 1.95–4.85 | 6.13 | NA | 4.77 |
| Turbidity | NTU | 240? | 43–220 | 360 | 17 | 800 |

(Continued)

TABLE 5-2 (Continued)
RESULTS OF FIELD AND PHYSICAL MEASUREMENTS

| Parameter | Units | Renkis Well<br>Bass Is. Form.<br>1982[b] | Hammermill #1<br>Bass Is. Form.<br>Pre-1964[a] | Other Wells<br>Oriskany Form.<br>1962[d] | West Penn.<br>Bass Is. Form.<br>1962[d] | Oilfield Brines<br>Oriskany Form.<br>1985[e] |
|---|---|---|---|---|---|---|
| Temperature (field) | °C | 19.5 | NA | NA | NA | NA |
| pH: | | | | | | |
| Field | pH units | NA | NA | NA | NA | 5.53-5.63 |
| Laboratory | pH units | 5.9 | NA | 6.5 | 2.35-7.8 | NA |
| Eh (field) | mV | NA | NA | NA | NA | (+141)-(+205) |
| Oxygen (dissolved) | mg/l | NA | NA | NA | NA | 0.2-1.5 |
| Specific Conductance: | | | | | | |
| Field | mmhos/cm @25°C | NA | NA | NA | NA | NA |
| Laboratory | mmhos/cm @25°C | NA | NA | 215 | 9.2-222 | 118-211 |
| Specific Gravity | | NA | 1.205 | 1.216 | 1.001-1.228 | 1.067-1.222 |
| Color: | | | | | | |
| Apparent | APHA Units | NA | NA | NA | NA | NA |
| True | APHA Units | NA | NA | NA | NA | NA |
| Residue: | | | | | | |
| Filterable (TDS) | g/l | NA | 229 | 294 | 6-312 | 101-343 |
| Nonfilterable (TSS) | g/l | NA | NA | NA | NA | NA |
| Turbidity | NTU | NA | NA | NA | NA | NA |

(Continued)

TABLE 5-2 (Continued)
RESULTS OF FIELD AND PHYSICAL MEASUREMENTS

| Parameter | Units | Hammermill Injection Liquor 1962[f] | Neutracel I Pulping Liquor 1983[g] | East H.S. Well Bass Is. Form. 1984[h] |
|---|---|---|---|---|
| Temperature (field) | °C | NA | NA | 24 |
| pH: | | | | |
| Field | pH units | NA | NA | 6.1 |
| Laboratory | pH units | 5.3 | 5.0 | 6.1 |
| Eh (field) | mV | NA | NA | NA |
| Oxygen (dissolved) | mg/l | NA | NA | NA |
| Specific Conductance: | | | | |
| Field | mmhos/cm @ 25°C | NA | NA | 352 |
| Laboratory | mmhos/cm @ 25°C | NA | 23 | 463–600 |
| Specific Gravity | | 1.02 | 1.06 | 1.204 |
| Color: | | | | |
| Apparent | APHA Units | NA | 20,000 | NA |
| True | APHA Units | NA | NA | NA |
| Residue: | | | | |
| Filterable (TDS) | g/l | 50 | 138 | 208 |
| Nonfilterable (TSS) | g/l | 0.225 | 0.260 | 749 |
| Turbidity | NTU | NA | 680 | NA |

Range of values are noted when multiple samplings/analyses are available.
Symbols and acronyms:
A question mark means barely legible values; results may not be the true analytical value.
NA = Not available.
ND = Not detected; detection limit was not available.

(Continued)

TABLE 5-2 (Continued)
RESULTS OF FIELD AND PHYSICAL MEASUREMENTS

[a] From attachments to Ecology and Environment (1982).
[b] From D'Appolonia/IT (1983).
[c] USGS laboratory pH measurement may be considered suspect when compared with other brine pH measurements.
[d] Originally Poth (1962). Ranges taken from D'Appolonia/IT (1983).
[e] From Dresel and Rose (1985). Data only from Oriskany Formation.
[f] From Dow Industrial Service (1962).
[g] Pulping liquor produced on a laboratory scale and analyzed by IT Corporation and Battelle. From D'Appolonia/IT (1984).
[h] From D'Appolonia/IT Corporation (1985). Values were consolidated from USGS and IT laboratory analyses.

from the Lockport Formation or the Bass Island Formation at Presque Isle. If brine from one of these formations is the original fluid that made up the seep, then the higher conductance would suggest an elevated concentration of the solution. This information does not agree with the composition of major ions in the samples.

The concentrations of major ions in the seep were comparable and not elevated over those of the brines from the Bass Island Formation. The contradiction between conductance and major ion chemistry may be explained by a number of factors. Variability may have been increased due to sampling and analysis artifacts. The analysis of samples with extremely high conductance frequently includes a dilution of the sample or calibration of the meter with high concentration standards. Information on the details of the field measurements was not available and therefore could not be further addressed.

Conductance is responsive to the qualitative composition as well as quantity of ions. For example, a solution with a given mass of sodium bromide would have a 39 percent lower conductance than a solution with the same mass of sodium chloride. Conductance measurements can be very useful in the context of monitoring a given fluid, but they should be used only as supportive evidence when evaluating unknown samples. Since there are influential elements (bromide) which were not measured and circumstances (precipitation products) which may have occurred, the conductance data alone cannot be used conclusively to show the origin or nature of the fluids.

Specific gravity is a measure of the mass of a given sample volume (relative to pure water). This value is generally proportional to the amount of dissolved material in a fluid. This relationship holds true for the seep and brine samples taken at the Presque Isle site. The seep and the Bass Island brine are similar in specific gravity (1.182-1.200 and 1.186-1.200, respectively) and filterable residue (269-295 g/l and 266 g/l, respectively). Since the brine from the Lockport Formation at

Presque Isle has a distinctively different specific gravity (1.136-1.152) and amount of filterable residue (203 g/l), this evidence is supportive of the earlier conclusion as to the origin of the seep (i.e., the Bass Island brine). As a general comparison, the specific gravity and filterable residue of the brines at Presque Isle are comparable to the local and regional subsurface brines. The Hammermill injection liquor and the Neutracel pulping liquor are significantly lower in specific gravity (1.02-1.06) than the brines at Presque Isle. Any dilution of the brines with the liquor would result in a slight decrease in the specific gravity. However, if the liquor was diluted 5 times with the Bass Island brine, the resultant specific gravity measurement would be indistinguishable from the background levels.

A general relationship is often apparent between the turbidity and the amount of nonfilterable residue in a sample. For the samples from Presque Isle, this relationship does not hold true, and no conclusions can be drawn from this data by itself. When the results of these measurements are compared with those of the pulping liquor and the East High School well, a scenario must be developed to explain the data. The concentration of nonfilterable residue in the liquor samples (0.225-0.260 g/l) is lower than the sample values from the Presque Isle site (1.95-6.13 g/l), but the East High School well (which is considered to be contaminated) had a very high concentration of nonfilterable residue (749 g/l).

In order for the pulping liquor to positively influence the East High School well, the particulates must have formed subsequent to the actual injection of the wastes. The possibility of post-injection reactions was suggested by earlier investigations. If the subsurface injection of pulping liquor physically or chemically creates particulates, then one would expect elevated levels of nonfilterable residue in the Bass Island brines at Presque Isle. This is difficult to evaluate, because there are no values available for other Bass Island brines. If the unfilterable residue in Lockport brine (6.13 g/l) at

Presque Isle is representative of other subsurface brines, there is no evidence for elevated particulates in the Bass Island (as might be created from the presence of pulping liquor).

There are two factors that would prevent the use of this analysis to assess the influence of the pulping liquor on the Bass Island brine. If the pulping liquor were diluted 100 times beyond that already occurring in the East High School brine, then the nonfilterable residue in the Bass Island brine at Presque Isle would be indistinguishable from the background. There is also the possibility that particulates were filtered out of the mixed brine solution en route to the Presque Isle site. Therefore the scenarios can explain how low levels of the pulping liquor may not be detected. Such speculation, however, cannot be used as conclusive evidence.

Color measurements can be useful in some investigations, but they are not very helpful in this evaluation. This is due in part to the lack of comparative information on related samples. The results might also have been beneficial if the complete spectra were available.

The redox potential (Eh) and dissolved oxygen concentration of a sample are indications of the oxidizing environment. This data can be useful in a qualitative evaluation, even though few sample analyses were available. The Eh values of the Bass Island brine (+110 mv) at Presque Isle and of the Oilfield brines (+141 to +205 mv) from the Oriskany Formation are indicative of slightly reducing to slightly oxidizing conditions. This is also suggested by the 0.2-1.5 mg/l of dissolved oxygen in the Oriskany brines. Under these conditions, some reduced iron and hydrogen sulfide may be present. The seep and the Lockport brines have moderately reducing conditions, as evidenced by their Eh values (-78 to -10 and -34 mv, respectively). Reduced iron and hydrogen sulfide should be prevalent in these samples. Such conditions are very difficult to measure accurately and precisely. Typically, there are chemical reactions that alter measurements and proceed in the time scale of minutes. These reactions may include pH changes, precipitate formation, and degassing activity that can concurrently change the resulting chemical composition of samples. Quick sampling and the possible use of "fixation" procedures are essential to the production of data suitable for evaluation of many compounds that can be influenced by these rapid reactions. These details are not available for this investigation. The uncertainty in the sampling and analysis procedures points out the need for cautious evaluation in certain data (such as iron sulfide).

### 5.4 Inorganics (Not Including Metals)

The results of inorganic analyses, excluding metals, can be found in Table 5-3. The data represent a summary of information from PADER, USGS, EPA, D'Appolonia/IT, Hammermill, and Dresel and Rose. The values were obtained from the references noted in the summary table.

Essentially all of the tabulated analyses were conducted on the 1982 samples from the Presque Isle site and the 1983 Neutracel I solution. However, very little information is available for a comparative evaluation. This severely limits the application of the data in this investigation. In addition, cyanides (total) and fluoride results are not helpful in this evaluation due to the low concentrations present in the samples. Many of the other compounds were intensively sampled and analyzed during 1982, but the analytical results between laboratories and different sampling events are highly variable. This variability also serves to hinder a complete evaluation. The ranges of values for many of the compounds suggest inconsistency in the sampling and analysis techniques. In some cases, sample heterogeneities or changes in composition with time may have contributed to some of the variation in the data.

The evaluation of acidity and alkalinity suffers from both the lack of comparative data and the large analytical variation. The similar acidity results for the seep (478-1070 mg $CaCO_3$/l) and the Bass Island brine (541 mg $CaCO_3$/l) at Presque Isle lends support to the theory that

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TABLE 5-3
INORGANIC ANALYSES (NOT INCLUDING METALS)

| Parameter | Units | Presque Isle Well | | | | |
|---|---|---|---|---|---|---|
| | | Seep 1979–1981[a] | Seep 1982[b] | Lockport Form. 1982[b] | Bass Is. Form. 1979–1981[a] | Bass Is. Form. 1982[b] |
| Acidity | mg/l–$CaCO_3$ | NA | 438–1070 | 44 | NA | 541 |
| Alkalinity | mg/l–$CaCO_3$ | 108? | 55–140 | 99–310 | 57?–106? | (<1[c]–1020)[d] |
| Cyanide (total) | mg/l | NA | <0.05–0.06 | <0.01–<0.05 | 0–0.03 | 0.03–<0.05 |
| Fluoride | mg/l | NA | 0.25–0.27 | 0.46 | 0 | 0.60–38[e] |
| NITROGEN: | | | | | | |
| Ammonia ($NH_3$) | mg/l–N | 400–532 | 90–440[e] | 48–82 | 465–506 | 438–568 |
| Total Kjeldahl | mg/l–N | NA | 276–408 | 6.5–67.2 | 460 | 470–569 |
| Nitrite ($NO_2$) | mg/l–N | 0.10 | <0.1–<0.1 | <0.1 | <0.01–0.06 | <0.1 |
| Nitrate ($NO_3$) | mg/l–N | 0.55 | <0.1–0.2 | 0.8 | <0.02–<0.08 | 3.6[e] |
| SULFUR: | | | | | | |
| Sulfide ($S^=$) | mg/l | NA | (24–764)[f] | (299–941)[f] | NA | (152–235)[f] |
| Sulfite ($SO_3$) | mg/l | NA | 9–18 | 11 | NA | 4 |
| Sulfate ($SO_4$) | mg/l | 4–<200 | (56–457)[d] | 660–1380 | <4–1400 | (93–1960)[d] |
| Phenols | mg/l | NA | 0.006–1.2 | 0.016–1 | NA | (0.031–1.438)[d] |
| Surfactants (MBA) | mg/l | NA | 0.05–0.60 | 0.05–0.05 | 0.11?–0.16? | 0.05 |
| Total Organic Carbon (TOC) | mg/l | 13 | 9–38 | 17–72 | 4.6–42 | 12–21 |
| OXYGEN DEMAND: | | | | | | |
| Biochemical ($BOD_5$) | mg/l | 250–630 | 51–>196 | 201–720 | 93–169 | (26–1120)[d] |
| Chemical (COD) | mg/l | NA | 7,490–13,000 | (1003–8600)[d] | 4,520?–7518? | (547–7,100)[d] |

(Continued)

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TABLE 5-3 (Continued)
INORGANIC ANALYSES (NOT INCLUDING METALS)

| Parameter | Units | Renkis Well Bass Is. Form. 1982[b] | Hammermill #1 Bass Is. Form. Pre-1964[a] | Other Wells Oriskany Form. 1962[g] | West Penn. Brines 1962[g] | Oilfield Brines Oriskany Form. 1985[h] |
|---|---|---|---|---|---|---|
| Acidity | mg/l-$CaCO_3$ | NA | NA | NA | NA | NA |
| Alkalinity | mg/l-$CaCO_3$ | 81 | NA | NA | NA | ND-318 |
| Cyanide (total) | mg/l | <0.01-<0.01 | NA | NA | NA | NA |
| Fluoride | mg/l | <0.1 | NA | 2.3 | NA | trace |
| NITROGEN: | | | | | | |
| Ammonia ($NH_3$) | mg/l-N | 530 | NA | NA | NA | NA |
| Total Kjeldahl | mg/l-N | NA | NA | NA | NA | NA |
| Nitrite ($NO_2$) | mg/l-N | NA | NA | NA | NA | NA |
| Nitrate ($NO_3$) | mg/l-N | NA | NA | NA | 0-118 | NA |
| SULFUR: | | | | | | |
| Sulfide ($S^=$) | mg/l | <0.1 | NA | NA | NA | 0.1-2.5 |
| Sulfite ($SO_3$) | mg/l | NA | NA | NA | NA | NA |
| Sulfate ($SO_4$) | mg/l | 52-93 | NA | 528 | 0-581 | ND-2.2 |
| Phenols | mg/l | 0.625 | NA | NA | NA | NA |
| Surfactants (MBA) | mg/l | NA | NA | NA | NA | NA |
| Total Organic Carbon (TOC) | mg/l | 470[e] | NA | NA | NA | NA |
| OXYGEN DEMAND: | | | | | | |
| Biochemical ($BOD_5$) | mg/l | 743 | NA | NA | NA | NA |
| Chemical (COD) | mg/l | 4,572 | NA | NA | NA | NA |

(Continued)

TABLE 5-3 (Continued)
INORGANIC ANALYSES (NOT INCLUDING METALS)

| Parameter | Units | Hammermill Injection Liquor 1962[j] | Neutracel I Pulping Liquor[i] 1983[d] | East H.S. Well Bass Is. Form. 1984[k] |
|---|---|---|---|---|
| Acidity | mg/l-$CaCO_3$ | 1900 | 12,800 | NA |
| Alkalinity | mg/l-$CaCO_3$ | 1500 | <1 | 141 |
| Cyanide (total) | mg/l | NA | <0.5 | NA |
| Fluoride | mg/l | NA | 0.78 | NA |
| NITROGEN: | | | | |
| Ammonia ($NH_3$) | mg/l-N | ND | 0.48 | NA |
| Total Kjeldahl | mg/l-N | NA | 7.5 | NA |
| Nitrite ($NO_2$) | mg/l-N | NA | <2.0 | NA |
| Nitrate ($NO_3$) | mg/l-N | NA | 190 | NA |
| SULFUR: | | | | |
| Sulfide ($S^=$) | mg/l | NA | 120 | NA |
| Sulfite ($SO_3$) | mg/l | NA | 3,500 | NA |
| Sulfate ($SO_4$) | mg/l | 17,500[l] | NA | 21 |
| Phenols | mg/l | NA | 16 | NA |
| Surfactants (MBA) | mg/l | NA | 1.8 | NA |
| Total Organic Carbon (TOC) | mg/l | NA | 48,400 | NA |
| OXYGEN DEMAND: | | | | |
| Biochemical ($BOD_5$) | mg/l | NA | 30,000 | NA |
| Chemical (COD) | mg/l | NA | 13,300 | NA |

Range of values are noted when multiple samplings and analyses are available.

Symbols and acronyms:

A question mark means barely legible report values; results may not be the true analytical value.

NA = Not available.

ND = Not detected; detection limit was not available.

[a]From attachments to Ecology and Environment (1982).

[b]From D'Appolonia/IT (1983).

[c]Value suspect due to low measured pH in the sample.

(Continued)

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TABLE 5-3 (Continued)
INORGANIC ANALYSES (NOT INCLUDING METALS)

[d]Significant variations exist in interlaboratory analyses and different sampling events.
[e]Suspect value. Value is much larger than those from comparable analyses.
[f]Different analytical methods were used. Sulfides were measured using EPA method 376.1 and a method employing a purge of acidified samples. Results were not always noted with method of analysis.
[g]Originally Poth (1962). Ranges taken from D'Appolonia/IT Interim Report, August 15, 1983.
[h]From Dresel and Rose (1985). Data from Oriskany Formation.
[i]Pulping liquor produced on a laboratory scale and analyzed by *IT Corporation* and Battelle.
[j]Dow Industrial Service (1962).
[k]From D'Appolonia/IT Corporation (1985).
[l]Total sulfur reported as sulfate.

the seep originated from the Bass Island Formation. There are no other data to show, however, whether the Bass Island brine at Presque Isle is contaminated or represents natural conditions; therefore, no other information can be drawn from the alkalinity data. The results do, however, draw attention to two points of interest that pertain to the liquor analyses. The acidity (1900 mg/l - $CaCO_3$) and the alkalinity (1500 mg/l - $CaCO_3$) of the injection liquor as reported in early analyses by Dow are nowhere near the values of the Neutracel I pulping liquor (12,800 mg/l - $CaCO_3$ Acidity, <1 mg/l - $CaCO_3$ Alkalinity) produced for EPA in 1983. The Neutracel I liquor, which was produced to duplicate the original liquor, may not be a reasonable approximation of the initial fluid. It is possible that differences in analytical techniques contribute to the confusion, but no evidence can be found to support this supposition.

The results for surfactant measurements (as MBAs) were low (0.05-0.60 mg/l) for most samples from Presque Isle. The only other MBAs measurement was of the Neutracel I pulping liquor (1.8 mg/l). If the Neutracel fluid represents the injection liquor (a supposition that was questioned previously) and acts in a conservative manner in geological formations, then a liquor dilution of 3- to 36-fold with brine would be necessary to account for the data. Given the uncertainties and the lack of comparable information, this conclusion cannot rest on its own merit and should only be used to support other evidence in the investigation.

Many of the inorganic compounds that were analyzed (containing N, P, and S, for example) are commonly involved in organic diagenesis reactions. Such processes would take place after the introduction of an organic rich material, such as pulping liquor, into the natural environment. These reactions, driven primarily by microbial activity, would result in the nonconservative distribution of many compounds. It is important to note that there is no hard evidence from this data to demonstrate diagenetic activity. Such evidence could have come from the evaluation of these compounds at a known contaminated site such as the

East High School well. Unfortunately, the only parameter analyzed at that location was sulfate (21 mg/l). The sulfate measurement, without the analyses of other sulfur species, is not sufficient to evaluate diagenesis and the concurrent reduction of oxidized compounds.

The following discussion is dependent on the presence of the pulping liquor at the site. It is presented here to provide a possible explanation for the concentrations of these geochemically active compounds. The aspect of organic diagenesis that is being considered is the oxidation of organic material by microorganisms for energy. The process utilizes oxidized compounds to react with organic matter (represented as $(CH_2O)_{106}\ (NH_3)_{16}\ (H_3PO_4))$ and creates a variety of reduced chemical species. Some generalized reactions that are thought to occur are shown below (taken from Froelich, 1979).

1. $(CH_2O)_{106}\ (NH_3)_{16}\ (H_3PO_4) + 138\ O_2 \rightarrow$
   $106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$

2. $(CH_2O)_{106}\ (NH_3)_{16}\ (H_3PO_4) + 84.8\ HNO_3 \rightarrow$
   $106\ CO_2 + 42.4\ N_2 + 16NH_3 + H_3PO_4 + 148.4\ H_2O$

3. $(CH_2O)_{106}\ (NH_3)_{16}\ (H_3PO_4) + 53\ SO_4{}^{2-} \rightarrow$
   $106\ CO_2 + 16\ NH_3 + 53\ S^{2-} + H_3PO_4 + 106\ H_2O$

The diagenetic reactions are believed to proceed in an order that gives the most energy to the microbial population. The equations are shown in decreasing order of "energy benefit" to the organisms.

In this process, oxygen, nitrites, nitrates, sulfites, and sulfates are reduced to form ammonia and hydrogen sulfides. As diagenesis proceeds, measurements of the total organic carbon and nitrogen, phenolics, and biochemical oxygen demand decreases. The chemical oxygen demand would not necessarily decrease drastically due to the formation of reduced chemical species. The lack of data and high levels of variability make it impossible to discern the diagenetic reactants and products of recent organic degradation from those occurring naturally in the past.

The data do indicate low or subaerobic conditions that could have resulted from oxidation and reduction reactions. If these reactions are occurring, the measurements of sulfides at the Presque Isle site may be strongly affecting the process. As shown earlier (see equation 3), sulfides can be formed from oxidized sulfur species. Sulfides can react with metals, such as iron, to produce metal sulfide precipitates or even be re-oxidized under different conditions to sulfates. When sulfide-rich fluids are exposed to the atmosphere, extremely fast degassing can occur. Since all of these possible reactions are probably transpiring simultaneously, subtle differences in sampling and analysis procedures can produce quite different results.

Sulfide results, however, do provide some general information. The data from Presque Isle samples show that the Lockport brines (299-941 mg $S^{=}$/l) are generally higher in sulfides than the Bass Island brines (152-235 mg $S^{=}$/l) and that the seep fluids have sulfide levels (24-764 mg $S^{=}$/l) comparable to both brines. There is evidence to suggest that the presence of sulfide in the Bass Island brines is not indicative of natural conditions. The lack of sulfide (<0.1 mg $S^{=}$/l) at the Renkis well and the low levels (0.1-2.5 mg $S^{=}$/l) in the Oriskany Formation, implies by reference that there is a perturbation in the natural chemistry in the Bass Island brine at Presque Isle.

While there is not enough sulfide in the initial pulping liquor (as measured in Neutracel solution, 120 mg $S^{=}$/l) to account for the measured concentrations in the Bass Island brine, sulfide could be produced from diagenetic reactions acting on the large amount of sulfite (Neutracel, 3,500 mg $SO_3^{=}$/l). Support for this theory could come from the measurement of sulfide at the East High School well. If sulfide concentrations exceeded natural levels, then the pulping liquor, which contaminates the Bass Island Formation at this location, could be presumed to be the causal agent. There are two problems with proving this theory. The first is due to the lack of sulfide data for this site. The second is the uncertainty as to the natural sulfide levels in Bass Island brines.

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D'Appolonia/IT-HML (3/83) has accumulated information on numerous wells from the Bass Island Formation that indicates the presence of "black water." This is a subjective term for the existence of sulfide in the fluids. Due to this possibility, the evaluation cannot be completed with regard to the sulfide information. There may be local heterogeneities in the Bass Island Formation that could account for the differences in the sulfide data. Acquiring quantitative sulfide information on Bass Island brines at nearby locations might help resolve the conflict.

## 5.5 Metals

A summary of the metal results can be found in Table 5-4. The data represent analytical results by PADER, USGS, EPA, D'Appolonia/IT, Dow, and Dresel and Rose. The data were obtained from the references noted in the summary table.

An evaluation of the data suffers from the same problems mentioned in earlier sections. There is a lack of comparative information, but more importantly, there is a large amount of variability in the results. In some cases, the problem may arise from the distinction between dissolved and total species. In other cases, there are very significant interlaboratory differences. As discussed in previous sections, this drastically limits the usefulness of the data.

For some metals, such as iron and copper, the observed variability may result from precipitation with sulfides, and therefore the results are not useful in this investigation. The total analyses of metals, such as aluminum and silica, are often susceptible to differences in sampling procedures. This is due to the possible presence of aluminosilicates in the well or subsequent contamination by clay-like materials. Concentrations of lead and zinc in samples can be altered easily by contamination sources in the field and in the laboratory. The high background level of salt in samples undoubtedly taxes the ability of the analytical procedure to prevent problems with interferences.

TABLE 5-4
RESULTS OF METALS ANALYSES

| Parameter | Units | Seep 1979-1981[a] | Seep 1982[b] | Presque Isle Well: Lockport Form. 1982[b] | Presque Isle Well: Bass Is. Form. 1979-1981[a,c] | Presque Isle Well: Bass Is. Form. 1982[b] |
|---|---|---|---|---|---|---|
| Aluminum | mg/l | NA | $4.6^T$ | $8.3^T$ | NA | $33.0^T$ |
| Antimony | mg/l | NA | <0.5-0.54($62^T$) | <0.5($53.5^T$) | 4.00 | <$0.5^D$(<0.5-95)$^T$ |
| Arsenic | mg/l | NA | <0.1-<0.1 | <0.1-<0.1 | 0-$16^d$ | <0.1-<0.1 |
| Beryllium | mg/l | NA | <0.1-<0.1 | <0.1-<0.1 | <0.072-0.09 | <0.1-0.1 |
| Cadmium | mg/l | NA | <0.001-<0.01 | <0.001-<0.01 | 0.003-1.9 | <0.001-0.4 |
| Chromium | mg/l | NA | <0.001-0.702 | 0.006-1.31 | 0.35-0.702 | <$0.001^D$-$2^T$ |
| Cobalt | mg/l | NA | 7.5 | 0.43 | 2.17-4.25 | 2.32-8.25 |
| Copper | mg/l | NA | 0.32-0.49 | 0.30-0.6 | 0.010-1.71 | (0.33-32)$^T$ |
| Iron | mg/l | 925 | ($2.0^D$-$440^T$)$^e$ | ($2.4^D$-$530^T$)$^e$ | ($4.8^D$-$95.5^T$)$^e$ | ($90^D$-$5000^T$)$^e$ |
| Lead | mg/l | NA | (<$0.001^D$-$74^T$)$^e$ | $0.001^D$-$4.2^T$ | 0.001-9.00 | (<$0.001^T$-$9.75^T$)$^e$ |
| Lithium | mg/l | NA | 180-240 | 32-37.5 | (154-1,800)$^e$ | 190-220 |
| Manganese | mg/l | NA | 0.73-1.9 | 1.4-3.1 | 0.67-1.5 | ($2.4^D$-$80^T$)$^e$ |
| Mercury | mg/l | NA | <0.001 | <0.001 | <0.0002-<$0.012^d$ | <0.001 |
| Nickel | mg/l | NA | 3.0-5.6 | 2.8-3.9 | 1.45-8.10 | 3.3-7.58 |
| Selenium | mg/l | NA | 0.67-1.20 | 0.39-1.10 | $12.0^d$ | 0.48-1.2 |
| Silica | mg/l | NA | $56^D$-$74^T$ | $31^D$-$1323^T$ | <10 | $15^D$-$434^T$ |
| Silver | mg/l | NA | <0.10-0.90 | <0.1-<0.1 | 0.33-1.00 | 0.17-0.27 |
| Thallium | mg/l | NA | <0.1-<0.1 | <0.1-<0.1 | 5.2 | <0.1-<0.1 |
| Titanium | mg/l | 0.750 | 0.93-1.6 | 0.77-2.3 | <1.0-12.1 | <1.0-2.0 |
| Zinc | mg/l | NA | $0.19^D$-$13.8^d$ | $0.15^D$-$2.1^T$ | 0.250-5.75 | $0.63^D$-$3.75^T$ |

(Continued)

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TABLE 5-4 (Continued)
RESULTS OF METALS ANALYSES

| Parameter | Units | Renkis Well Bass Is. Form. 1982[b] | Hammermill #1 Bass Is. Form. Pre-1964[a] | Other Wells Oriskany Form. 1962[f] | West Penn. Bass Is. Form. 1962[f] | Oilfield Brines Oriskany Form. 1985[g] |
|---|---|---|---|---|---|---|
| Aluminum | mg/l | $0.4^{T}$ | NA | 30 | NA | NA |
| Antimony | mg/l | $79.3^{T}$ | NA | NA | NA | NA |
| Arsenic | mg/l | NA | NA | NA | NA | NA |
| Beryllium | mg/l | NA | NA | NA | NA | NA |
| Cadmium | mg/l | <0.01 | NA | NA | NA | NA |
| Chromium | mg/l | $0.59^{D}$–$1.0^{T}$ | NA | NA | NA | NA |
| Cobalt | mg/l | $6.25^{T}$–$200^{D,e}$ | NA | NA | NA | NA |
| Copper | mg/l | 0.250–1.25 | NA | 0.15 | 0–2.8 | 0.01–0.05 |
| Iron | mg/l | $(7.9^{D}$–$147^{T})^{e}$ | NA | 3.9 | 0.13–290 | 207–458 |
| Lead | mg/l | $(3.5^{D}$–$10.25^{T})^{e}$ | NA | NA | NA | ND–0.02 |
| Lithium | mg/l | 170–208 | NA | 187 | 0–219 | 105–315 |
| Manganese | mg/l | 3.5–5.75 | NA | 1.70 | 0.04–31 | 5.6–6.2 |
| Mercury | mg/l | NA | NA | NA | NA | NA |
| Nickel | mg/l | 5.75 | NA | NA | NA | NA |
| Selenium | mg/l | 3.95 | NA | NA | NA | NA |
| Silica | mg/l | NA | NA | NA | NA | NA |
| Silver | mg/l | 1.0 | NA | NA | NA | NA |
| Thallium | mg/l | NA | NA | NA | NA | NA |
| Titanium | mg/l | <1.0 | NA | NA | NA | NA |
| Zinc | mg/l | $7.0^{D}$–$13.0^{T}$ | NA | 2.0 | NA | 0.03–1.26 |

(Continued)

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TABLE 5-4 (Continued)
RESULTS OF METALS ANALYSES

| Parameter | Units | Hammermill Injection Liquor 1962[h] | Neutracel I Pulping Liquor 1983[i] | East H.S. Well Bass Is. Form. 1984[j] |
|---|---|---|---|---|
| Aluminum | mg/l | NA | 1.1 | NA |
| Antimony | mg/l | NA | <0.8 | NA |
| Arsenic | mg/l | NA | <0.7 | <0.010 |
| Beryllium | mg/l | NA | <0.05 | <0.050 |
| Cadmium | mg/l | NA | <0.02 | 0.390 |
| Chromium | mg/l | NA | 0.35 | 0.420 |
| Cobalt | mg/l | NA | <0.1 | 4.10 |
| Copper | mg/l | NA | 1.1 | NA |
| Iron | mg/l | 6 | 9 | 15 |
| Lead | mg/l | NA | <0.7 | 4.40 |
| Lithium | mg/l | NA | <0.04 | 180 |
| Manganese | mg/l | NA | 2.9 | 9.1 |
| Mercury | mg/l | NA | <0.03 | 0.155 |
| Nickel | mg/l | NA | 0.42 | NA |
| Selenium | mg/l | NA | <0.9 | <0.010 |
| Silica | mg/l | NA | 1,560 | NA |
| Silver | mg/l | NA | <0.05 | NA |
| Thallium | mg/l | NA | <0.05 | NA |
| Titanium | mg/l | NA | <0.05 | NA |
| Zinc | mg/l | NA | 2.0 | 36 |

*Range of values are noted when multiple samplings and analyses were available. The ranges are* inclusive of total and dissolved analyses when available. Significant deviations between the components are footnoted.

(Continued)

TABLE 5-4 (*Continued*)
RESULTS OF METALS ANALYSES

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Acronyms:
A question mark means barely legible report values; results may not be the true analytical value.
NA = Not available
ND = Not detected; detection limit was not available
T = Total analysis
D = Dissolved analysis

[a]From attachments to Ecology and Environment (1985).
[b]From D'Appolonia/IT (1983).
[c]USGS values of "zero" were thrown out, as their meaning was uncertain.
[d]Suspect value. *The value is much larger than those from comparable* analyses.
[e]Significant variations exist in interlaboratory analyses and different sampling events.
[f]Originally Poth (1962). Ranges of values were taken from D'Appolonia/IT Interim Report, August 15, 1983.
[g]Dresel and Rose (1985). Data from Oriskany Formation.
[h]Dow Industrial Service (1962).
[i]Pulping liquor produced on a laboratory scale and analyzed by IT Corporation and Battelle. From D'Appolonia (1984).
[j]From D'Appolonia/IT (1985).

The lack of consistent, comparable data and the low levels of some metals observed in samples produced information that is highly suspect. The sole exception is lithium, which probably should have been considered in the context of the major ions. The lithium data add to the evidence for the Bass Island brine origin for the seep. The Bass Island brine at Presque Isle has lithium concentrations roughly equivalent to those in Bass Island brines from the Renkis and East High School wells. The comparison of the data with the contaminated East High School well information again points out an important consideration. In order for a contaminant fluid to be observed, its chemical composition in the natural fluid has to exceed the variability in a measured parameter.

In at least one report (i.e., Ecology and Environment, 1982), there was discussion of the presence of compounds indicative of the pulping industry. Compounds such as titanium probably were not associated with the particular fluids that were deeply injected. Furthermore, such compounds, which are very useful in sorting out possible influences, should not be used in lieu of comparable data (if available). However, some of the more exotic chemicals may serve as useful evidence if background levels are exceeded. This apparently was not the case for the pulping liquor.

5.6 Volatile Organic Compounds

The results from analyses of volatile organic compounds can be found in Table 5-5. The analyses were performed by EPA, USGS, D'Appolonia/IT, ETC, and Battelle. The data were obtained from the references noted in the summary table.

From the data available, there seems to be significant interlaboratory variation. In some cases, the agreement is quite good, as shown by the benzene determination in the seep samples (110 ug/l, EPA laboratory vs. 105 ug/l, D'Appolonia/IT laboratory). However, the benzene analyses of the Bass Island brine at Presque Isle demonstrate poor consistency between the laboratories. This variation should be considered when evaluating the data.

TABLE 5-5
RESULTS OF VOLATILE COMPOUNDS ANALYSES

| Compound | Units | Presque Isle Well: Seep, October 18, 1982: EPA[a] | Seep, October 18, 1982: D'Appolonia[a] | Bass Island Formation, November 10, 1982: EPA | Bass Island Formation, November 10, 1982: USGS[a] | Bass Island Formation, November 10, 1982: D'Appolonia[a] |
|---|---|---|---|---|---|---|
| **Priority Volatiles** | | | | | | |
| Benzene | ug/l | 110 | 105 | 81 | 300 | 124 |
| Chloroform | ug/l | ND | ND | ND | ND | ND |
| Ethylbenzene | ug/l | 5.8 | 2 | 2.3 | ND | 2 |
| Methylene Chloride | ug/l | ND | ND | ND | ND | ND |
| 1,1,1-Trichloroethane | ug/l | ND | ND | ND | ND | ND |
| Toluene | ug/l | 40 | 34 | ND | 16 | 38 |
| Trichloroethylene | ug/l | ND | ND | ND | ND | ND |
| Tetrachloroethene | ug/l | ND | ND | ND | ND | ND |
| trans-1,3-Dichloropropene | ug/l | ND | ND | ND | ND | 6 |
| **Additional Volatiles** | | | | | | |
| Xylenes | ug/l | 20-200 | — | 2-20 | — | — |
| Acetone | Qualitative, (ug/l)[b] | — | — | * | — | — |
| Cyclohexane | Qualitative, (ug/l)[b] | — | — | ND | — | — |
| Hexane | Qualitative, (ug/l)[b] | — | — | + | — | — |
| Methyl cyclohexane | Qualitative, (ug/l)[b] | + | — | + | — | — |
| Nonane | Qualitative, (ug/l)[b] | — | — | + | — | — |
| Pentane | Qualitative, (ug/l)[b] | — | — | + | — | — |
| Tetrahydrofuran | Qualitative, (ug/l)[b] | — | ND | * | — | + |
| Carbon Disulfide | Qualitative, (ug/l)[b] | — | — | — | — | — |

(Continued)

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TABLE 5-5 (Continued)
RESULTS OF VOLATILE COMPOUNDS ANALYSES

| Compound | Units | Renkis Well, Bass Island Formation, December 11, 1982 | | Neutracel I, Pulping Liquor[c] | | East High School Well, Bass Island Formation, September 13, 1984 |
|---|---|---|---|---|---|---|
| | | EPA[a] | USGS[a] | ETC[c] | Battelle[c] | IT[d] |
| **Priority Volatiles** | | | | | | |
| Benzene | ug/l | * | 25 | ND | — | 1.8 |
| Chloroform | ug/l | * | 62 | ND | — | <1.0 |
| Ethylbenzene | ug/l | * | 32 | <10,000 | — | <1.0 |
| Methylene Chloride | ug/l | ND | 34 | 14,600 | <1,000[e] | <10.0 |
| 1,1,1-Trichloroethane | ug/l | 1.6 | ND | <10,000 | — | <1.0 |
| Toluene | ug/l | * | 150 | 12,300 | <1,000[e] | 1.5 |
| Trichloroethylene | ug/l | 1.4 | ND | <10,000 | — | <1.0 |
| Tetrachloroethene | ug/l | 14[f] | ND | <10,000 | — | <1.0 |
| trans-1,3-Dichloropropene | ug/l | ND | ND | ND | — | <1.0 |
| **Additional Volatiles** | | | | | | |
| Xylenes | ug/l | * | — | 22,800 | — | ND |
| Acetone | Qualitative, (ug/l)[b] | * | — | <100,000 | — | <10 |
| Cyclohexane | Qualitative, (ug/l)[b] | + | — | <10,000 | — | ND |
| Hexane | Qualitative, (ug/l)[b] | + | — | <10,000 | — | ND |
| Methyl cyclohexane | Qualitative, (ug/l)[b] | + | — | <10,000 | — | ND |
| Nonane | Qualitative, (ug/l)[b] | + | — | <10,000 | — | ND |
| Pentane | Qualitative, (ug/l)[b] | * | — | <10,000 | — | ND |
| Tetrahydrofuran | Qualitative, (ug/l)[b] | ND | — | <100,000 | — | ND |
| Carbon Disulfide | Qualitative, (ug/l)[b] | — | — | — | — | 1.5 |

Symbols and acronyms:
Asterisk indicates significant blank interference; value is suspect.
Plus sign indicates positive determination of compound or group.
Two dashes indicate analysis was not performed, or the data was not reported.
ND = Not detected. Detection limit was not available.
NA = Not available.

(Continued)

TABLE 5-5 (Continued)
RESULTS OF VOLATILE COMPOUNDS ANALYSES

[a] From D'Appolonia/IT (1983).
[b] Quantified results are reported in ug/l when data is available.
[c] Pulping liquor was produced on a laboratory scale and analyzed by ETC and Battelle. From D'Appolonia/IT (1984).
[d] From Appolonia/IT Corporation (1985).
[e] Results represent a re-analysis of a sample not preserved for volatiles.
[f] Analysis not corrected for positive blank value.

Another factor that limits the usefulness of the results involves detection limits. The reporting of a compound as "not detected" (ND) is not helpful to the evaluation if the detection limits between laboratories or samples are not similar. The results for the Neutracel I pulping liquor and the Bass Island brine from the East High School well could not be fully evaluated due to the reporting differences. The D'Appolonia/IT-HML report (8/31/84), referencing the Neutracel I analyses by ETC, utilized the distinction between "below minimum detection limit" (BMDL) and "not detected" (ND) to not report the detection limits (usually <10,000 ug/l) by ETC.

While BMDL does serve a purpose in signifying the presence of a compound, the loss of the detection limit value is very misleading in a quantitative evaluation. These detection limits were undoubtedly available for the D'Appolonia/IT report (1984) and were used in Table 5-5. A similar loss of information occurred in the D'Appolonia/IT report (HML, 3/85) during a technical review of EPA documents. In their summary table, D'Appolonia/IT did not report the detection limit value, which in this case ranged from <1 to <10 ug/l. When data from the two reports are compared, an analytical detection limit of 10,000 ug/l could hide the presence of a compound at 1,000 ug/l but not when the analytical detection limit is 1 ug/l.

The high detection limits on the analyses of the Neutracel I fluid seem somewhat excessive. Although such decisions are always made easier after the fact, a dilution of the fluid by 10-50 times less than what was used could have increased information about compounds without introducing unmanageable organic contamination. The problems with inconsistencies in the detection limits and the use of qualitative notations limits the usefulness of the data on "additional" volatiles.

The majority of the volatile compounds that were detected are often associated with petroleum products. The geological formations in question were explored for development of hydrocarbon resources, and their presence is not unusual. If volatile concentrations were found to be elevated over those found in the background brines, then the results might serve as evidence connecting the pulping liquor to the problems at the Presque Isle site. The other information needed to complete the evidence is the presence of the compound in the pulping liquor and in the Bass Island brine at the East High School well. The data do not decisively prove any of the factors mentioned above. The uncontaminated Renkis well brine has volatile organic concentrations frequently in excess of those at the Presque Isle and East High School well. Given this fact and the high detection limits for the Neutracel I analyses, a comparative evaluation of the volatile organic results cannot be used to prove or disprove the presence of the pulping wastes at the Presque Isle site.

### 5.7 Semivolatile and Tentatively Identified Compound (TIC) Groups

The results of the semivolatile analyses can be found in Table 5-6. The analytical data was reported by EPA, D'Appolonia/IT, and ETC. The data were obtained from the references noted in the summary table.

The data evaluation suffers from the same problems noted for the volatile organic results in Section 5.6. There is significant interlaboratory variation and uncertainties in the detection limits. These factors and the limited information derived from the TIC groups prevent useful conclusions being drawn from the majority of the results.

Phenol was found in the Neutracel I pulping liquor at a concentration of 621 ug/l, but it was not found at a concentration above 1 ug/l in the Bass Island brine at the contaminated East High School well site. This suggests a minimum of a 621:1 dilution of the pulping liquor with the brine if the phenol acts conservatively. Since phenol was not present at significant levels in the brine samples, it is possible that this dilution represents a reasonable approximation of the true mixture at the East High School well. D'Appolonia/IT (HML, 3/85) calculated possible dilution ratios of the pulping liquor with brine at the Presque

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TABLE 5-6
SEMIVOLATILE AND TENTATIVELY IDENTIFIED COMPOUND (TIC) GROUPS

| Compound | Units | Presque Isle Well[a] Seep October 18, 1982 EPA | Presque Isle Well[a] Seep October 18, 1982 D'Appolinia | Presque Isle Well[a] Bass Island Formation November 10, 1982 EPA | Presque Isle Well[a] Bass Island Formation November 10, 1982 USGS | Presque Isle Well[a] Bass Island Formation November 10, 1982 D'Appolonia |
|---|---|---|---|---|---|---|
| **Base/Neutral Extractables** | | | | | | |
| Acenaphthene | ug/l | 1.07 | 1 | ND | -- | ND |
| Anthracene | ug/l | 5.65 | ≤27 | ND | -- | ND |
| Benzo(a)anthracene | ug/l | 7.30 | ≤8 | ND | -- | ND |
| Benzo(b)fluoranthene | ug/l | 3.81 | ND | ND | -- | ND |
| Benzo(k)fluoranthene | ug/l | 4.37 | ND | ND | -- | ND |
| Benzo(a)pyrene | ug/l | 4.04 | ND | ND | -- | ND |
| Benzo(ghi)perylene | ug/l | 0.91 | ND | ND | -- | ND |
| Bis(2-Ethylhexyl)phthalate | ug/l | ND | ND | 14.14 | -- | ND |
| Chrysene | ug/l | 6.62 | ≤8 | ND | -- | ND |
| Di-N-Butylphthalate | ug/l | * | ND | * | -- | ND |
| Di-ethylphthalate | ug/l | ND | 2 | ND | -- | ND |
| Fluoranthene | ug/l | 29.0 | 20 | 0.76 | -- | ND |
| Fluorene | ug/l | ND | 3 | ND | -- | ND |
| Indeno(1,2,3-cd)Pyrene | ug/l | 1.37 | ND | ND | -- | ND |
| Naphthalene | ug/l | 2.39 | ND | 1.24 | -- | ND |
| Phenanthrene | ug/l | 35.3 | ≤27 | 1.03 | -- | ND |
| Pyrene | ug/l | 22.9 | 13 | 0.60 | -- | ND |
| **Acid Extractable** | | | | | | |
| 2,4-Dimethylphenol | ug/l | 1.57 | ND | ND | -- | ND |
| Phenol | ug/l | * | ND | * | -- | ND |
| **TIC Groups** | | | | | | |
| Aromatic Hydrocarbons (HCs) | Qualitative | + | + | + | -- | + |
| Branched chain HCs | Qualitative | + | + | + | -- | + |
| Straight chain HCs | Qualitative | + | + | + | -- | + |
| Alkenes | Qualitative | -- | -- | + | -- | -- |
| Ketones | Qualitative | -- | ND | + | -- | + |
| Hydroxylamine | Qualitative | -- | -- | -- | -- | -- |
| Hydrated Napthalene | Qualitative | -- | -- | -- | -- | -- |
| Cyclic Hydrocarbons | Qualitative | + | -- | + | -- | + |
| Organo Sulfur | Qualitative | + | + | + | -- | + |
| Aromatic Sulfonamide | Qualitative | -- | ND | + | -- | ND |
| Mercaptans | Qualitative | + | + | + | -- | + |
| Straight-chain Carboxlic Acids | Qualitative | -- | -- | -- | -- | -- |

(Continued)

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TABLE 5-6 (Continued)
SEMIVOLATILE AND TENTATIVELY IDENTIFIED COMPOUND (TIC) GROUPS

| Compound | Units | Renkis Well[a] Bass Island Formation December 11, 1982 EPA | Renkis Well[a] USGS | Neutracel I[b] Pulping Liquor ETC/Battelle | East H.S. Well[c] Bass Island Formation September 13, 1984 IT |
|---|---|---|---|---|---|
| **Base/Neutral Extractables** | | | | | |
| Acenaphthene | ug/l | ND | -- | <100 | ND |
| Anthracene | ug/l | ND | -- | <100 | ND |
| Benzo(a)anthracene | ug/l | ND | -- | <100 | ND |
| Benzo(b)fluoranthene | ug/l | ND | -- | <100 | ND |
| Benzo(k)fluoranthene | ug/l | ND | -- | <100 | ND |
| Benzo(a)pyrene | ug/l | ND | -- | <100 | ND |
| Benzo(ghi)perylene | ug/l | ND | -- | <100 | ND |
| Bis(2-Ethylhexyl)phthalate | ug/l | ND | -- | <100 | ND |
| Chrysene | ug/l | ND | -- | <100 | ND |
| Di-N-Butylphthalate | ug/l | * | -- | <100 | ND |
| Di-ethylphthalate | ug/l | ND | -- | <100 | ND |
| Fluoranthene | ug/l | ND | -- | <100 | ND |
| Fluorene | ug/l | ND | -- | <100 | ND |
| Indeno(1,2,3-cd)Pyrene | ug/l | ND | -- | <100 | ND |
| Naphthalene | ug/l | ND | -- | <100 | ND |
| Phenanthrene | ug/l | ND | -- | <100 | ND |
| Pyrene | ug/l | ND | -- | <100 | ND |
| **Acid Extractable** | | | | | |
| 2,4-Dimethylphenol | ug/l | ND | -- | <250 | ND |
| Phenol | ug/l | 0.95 | -- | 621 | ND |
| **TIC Groups** | | | | | |
| Aromatic Hydrocarbons (HCs) | Qualitative | + | -- | + | + |
| Branched chain HCs | Qualitative | + | -- | + | ND |
| Straight chain HCs | Qualitative | + | -- | -- | ND |
| Alkenes | Qualitative | + | -- | -- | -- |
| Ketones | Qualitative | + | -- | + | ND |
| Hydroxylamine | Qualitative | + | -- | -- | -- |
| Hydrated Napthalene | Qualitative | + | -- | -- | -- |
| Cyclic Hydrocarbons | Qualitative | + | -- | + | ND |
| Organo Sulfur | Qualitative | + | -- | -- | + |
| Aromatic Sulfonamide | Qualitative | ND | -- | -- | ND |
| Mercaptans | Qualitative | + | -- | -- | ND |
| Straight-chain Carboxlic Acids | Qualitative | -- | -- | NA | + |

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(Continued)

TABLE 5-6 (Continued)

SEMIVOLATILE AND TENTATIVELY IDENTIFIED COMPOUND (TIC) GROUPS

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Symbols and acronyms:
Asterisk indicates significant blank interference; value is suspect.
Plus sign indicates positive determination of compound or group.
Two dashes indicates analysis was not performed or the data was not reported.
ND = Not detected; detection limit was not available.
NA = Not available.

[a]Data from D'Appolonia/IT (1983).
[b]Pulping liquor was produced on a laboratory scale and analyzed by ETC and Battelle (data from D'Appolonia/IT, (1983).
[c]Data from D'Appolonia/IT (1985).

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Isle site, but they utilized compounds that were volatile, could be influenced by geological filtration, and were biological and chemically reactive period. For some compounds, the results were highly variable and could account for large differences in the dilution ratios.

5.8 Target Compounds

The results of the available analyses for target compounds can be found in Table 5-7. This data was separated from other results, because the compounds were thought to have special significance or association with pulping liquor. The data were obtained from the references noted in the summary table.

The first 18 compounds in Table 5-7 are thought to be associated with pulping activities. The approach was to determine the presence of these compounds in the samples, which would indicate influence of the pulping waste at that site. While this approach may have been valid if one assumed that these were part of the injection liquor, the implementation of the concept has difficulties. An evaluation of the presence of a compound is directly affected by the analytical detection limit. The higher the sensitivity (and lower the detection limit), the higher the likelihood that a trace compound will be detected. Since the data are represented as qualitative information and no detection limits are presented, the evaluation is severely hampered. If one assumes comparable detection limits in all samples, then the data do not show the presence of these specific compounds, and thus pulping liquor in the environment. However, without quantitative information, the data are of limited use in the investigation. It is surprising that more of these compounds were not analyzed or reported in the Neutracel I pulping liquor and the East High School well brine.

Thurman (1986) reviewed numerous papers (Matsumoto et al., 1977; Larson, 1978; Suffet et al., 1980; Mycke, 1982; Matsumoto and Hanya, 1980; and Kawamura and Kaplan, 1983) in which many of these aromatic acids were found at low microgram-per-liter concentrations in

TABLE 5-7
RESULTS OF ANALYSES OF TARGET COMPOUNDS

| Compound | Units | Presque Isle Well[a] Seep October 18, 1982 EPA | Seep October 18, 1982 D'Appolinia | Bass Island Formation November 10, 1982 EPA | Bass Island Formation November 10, 1982 USGS | Bass Island Formation November 10, 1982 D'Appolonia | Bass Island Formation November 5, 1982 D'Appolonia |
|---|---|---|---|---|---|---|---|
| Catechol | Qualitative | — | — | — | — | — | — |
| Vanillin | Qualitative | ND | — | — | — | — | — |
| Syringaldehyde | Qualitative | ND | — | — | — | — | — |
| Acetosyringone | Qualitative | ND | — | — | — | — | — |
| Abietic Acid | Qualitative | ND | ND | — | — | ND | — |
| Dehydroabietic Acid | Qualitative | ND | ND | — | — | ND | — |
| Isopimaric Acid | Qualitative | ND | ND | — | — | ND | — |
| Pimaric Acid | Qualitative | ND | ND | — | — | ND | — |
| Oleic Acid | Qualitative | * | ND | — | — | ND | — |
| Linoleic Acid | Qualitative | — | ND | — | — | ND | — |
| Linolenic Acid | Qualitative | — | ND | — | — | ND | — |
| 9,10-Epoxystearic Acid | Qualitative | — | ND | — | — | ND | — |
| Epoxystearic Acid | Qualitative | — | ND | — | — | ND | — |
| 9,10-Dichlorostearic Acid | Qualitative | — | ND | — | — | ND | — |
| Monochlorodehydroabietic Acid | Qualitative | — | ND | — | — | ND | — |
| Dichlorodehydroabietic Acid | Qualitative | — | ND | — | — | ND | — |
| 3,4,5-Trichloroguaiacol | Qualitative | ND | ND | — | — | ND | — |
| Tetrachloroguaiacol | Qualitative | ND | ND | — | — | ND | — |
| Acetate | mg/l | — | <1.0 | — | — | <0.5 | — |
| Formate | mg/l | — | 9.0 | — | — | 8.7 | — |
| Tannin-Lignin | mg/l | — | <2.0 | — | 38 | <2.0 | <2.0 |

(Continued)

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TABLE 5-7
RESULTS OF ANALYSES OF TARGET COMPOUNDS

| Compound | Units | Renkis Well[a] Bass Island Formation December 11, 1982 | | Neutracel I[b] Pulping Liquor | East H.S. Well[c] Bass Island Formation September 13, 1984 | |
|---|---|---|---|---|---|---|
| | | EPA | USGS | ETC/Battelle | USGS | IT |
| Catechol | Qualitative | — | — | — | — | ND |
| Vanillin | Qualitative | — | — | + | — | ND |
| Syringaldehyde | Qualitative | — | — | + | — | ND |
| Acetosyringone | Qualitative | — | — | — | — | ND |
| Abietic Acid | Qualitative | — | — | — | — | ND |
| Dehydroabietic Acid | Qualitative | — | — | — | — | ND |
| Isopimaric Acid | Qualitative | — | — | — | — | ND |
| Pimaric Acid | Qualitative | — | — | — | — | ND |
| Oleic Acid | Qualitative | — | — | — | — | ND |
| Linoleic Acid | Qualitative | — | — | — | — | ND |
| Linolenic Acid | Qualitative | — | — | — | — | ND |
| 9,10-Epoxystearic Acid | Qualitative | — | — | — | — | ND |
| Epoxystearic Acid | Qualitative | — | — | — | — | ND |
| 9,10-Dichlorostearic Acid | Qualitative | — | — | — | — | ND |
| Monochlorodehydroabietic Acid | Qualitative | — | — | — | — | ND |
| Dichlorodehydroabietic Acid | Qualitative | — | — | — | — | ND |
| 3,4,5-Trichloroguaiacol | Qualitative | — | — | — | — | ND |
| Tetrachloroguaiacol | Qualitative | — | — | — | — | ND |
| Acetate | mg/l | — | — | 11,000 - 12,000 | — | 270 |
| Formate | mg/l | — | — | 50 | — | <20 |
| Tannin-Lignin | mg/l | — | 73 | 96,000 - 100,000 | 206 | 520 |

Symbols and acronyms:
Asterisk means that the range of values is noted when multiple samplings or analyses were available.
Two dashes indicate that an analysis was not performed or the data was not reported.
Plus sign indicates a positive determination of compound or group.
ND = Not detected; the detection limit was not available.

[a]Data from D'Appolonia/IT (1983).
[b]Pulping liquor was produced on a laboratory scale and analyzed by ETC and Battelle (from D'Appolonia/IT, 1984).
[c]Data from D'Appolonia/IT (1985).

environmental samples. Several of these research investigations were involved in evaluating the influence of organic matter degradation. If the Presque Isle and pulping waste samples had been analyzed for these compounds at low concentrations, then some beneficial information may have resulted.

Analyses for the two volatile fatty acids, expressed as acetate and formate, also presented the possibility of tracing the pulping liquor in the natural brines. The principal assumptions of the approach as expressed by D'Appolonia/IT were that these compounds act conservatively and exist in a ratio of approximately 10 acetate:1 formate (D'Appolonia/IT-HML, 8/31/84). Analyses of the Neutracel I pulping liquor (~11,500 acetate:50 formate) yielded a ratio of 230:1, which greatly exceeds the expected ratio but may indicate the range of values that could exist due to changes in wood composition.

The acetate (270 mg/l) to formate (<20 mg/l) ratio of greater than 13.5:1 in the brine from the East High School well was used to demonstrate the presence of the pulping liquor at the site. Acetate to formate ratios in the Presque Isle samples from the Lockport Formation (<0.16:1), Bass Island Formation (<0.06:1), and the seep (<0.11:1) demonstrate a reversal in the abundance of the two compounds. By itself, the data represents the strongest case against the presence of pulping waste at the Presque Isle site.

There are two problems associated with the volatile fatty acid evidence: (1) without analyses for the Renkis well sample, the results for the Presque Isle samples cannot be compared to background concentrations, and (2) the volatile fatty acids may not act conservatively. Since these compounds are typically produced by the microbial oxidation of dissolved and particulate organic carbon, they undoubtedly will continue to degrade. To further complicate the issue, degradation probably does not proceed equally on the two compounds. The volatile fatty acids, formic acid and acetic acid,

```
       O                    H   O
       ||                   |   ||
   H - C - OH           H - C - C - OH
                            |
                            H

   Formic Acid           Acetic Acid
```

are different by one carbon atom, the C - C bond represents an additional location for possible microbial attack.

If the C - C bond of the acetic acid molecule is broken before the carboxylic acid is attacked, a formic acid molecule is created. Therefore, it is possible during these activities to reverse the acetate/formate ratio. This possibility is only presented as another explanation of the data. A change in the ratios to those observed at the Presque Isle site could be explained by longer residence times allowing extended degradation.

Information on the tannin and lignin concentrations in the samples could have been very useful in evaluating the presence of the pulping wastes. However, there are several points of concern regarding the data. D'Appolonia/IT-HML (8/31/84) summarized some of the problems associated with the analyses. The ultraviolet (UV) spectrophotometric technique is a measure of hydroxylated aromatic compounds and simpler phenolic compounds. The analyses, therefore, are not specific for tannin or lignin. In addition to the nonspecificity, D'Appolonia/IT (1983) found severe positive analytical interferences. In spite of this, no attempts were noted to resolve this problem. Such corrective procedures might have included standard addition techniques.

The UV method of analysis may be a reasonable measure of lignin in spent pulping liquor, since the lignin undoubtedly constitutes the majority of any phenolic compounds. The use of the technique on brine samples produces results that can be influenced by other UV absorbing compounds that may be prevalent. In general, the net effect probably would be artificially nigh lignin values in the brine and seep samples.

The use of this observation as conclusive evidence for or against the pulping liquor presence at Presque Isle would be inappropriate due to uncertainties in the sampling and analysis procedures.

The low solubility of lignin could introduce artifacts from the sampling and analysis procedures. An unknown that would influence the solubility is the percentage of lignosulfonate of the lignin in the pulping liquor. Lignosulfonate probably constitutes the majority of the lignin species initially and its' presence would result in relatively high solubility of the compound in the initial pulping liquor. Analysis of a sample of the pulping liquor probably would be a reasonably accurate measurement of lignin compounds.

During natural degradation processes, the lignin in the waste may be de-sulfonated. If this occurred, the solubility of the resultant lignin macromolecule would be significantly decreased. Sampling activities that involved normal filtration procedures (0.22 - 5 micron effective pore size) would remove lignin that would now be associated with solid particles in the liquid sample. The fact that the pulping wastes were filtered through 110-mesh material would not influence the above observation. The particles resulting from this filtration activity could be as large as 125 microns. This would be reduced by the inclusion of diatomaceous filtration material, but a significant amount of particulates would still exist. The net result is a large amount of lignin compounds that would pass through the pre-injection filtration and later be removed during the sampling or pre-analysis filtration. This would result in artificially low values for the natural samples.

In spite of the observed potential for problems in the tannin-lignin (T-L) analyses, the positive results (206 - 520 mg T-L/l) noted for brine samples from the East High School well are considered to be supportive evidence for the presence of pulping wastes at this site. With the sampling and analytical difficulties in mind, the observations can provide the basis of a discussion concerning the diluted presence of the pulping liquor at this site. If the tannin-lignin values are proportional to the pulping waste and the compounds act conservatively, one part of the pulping waste would be diluted with 270 parts of brine at the East High School well. Average values are used in this calculation of the ratio. It is impossible to estimate whether this ratio represents a maximum or a minimum value, due to the sampling and analysis difficulties as well as the probable nonconservative behavior of the tannins and lignins. Extending this discussion to the Presque Isle site is even more difficult.

An evaluation of the other tannin-lignin results in Table 5-7 reveals a large interlaboratory variation. The USGS measured 38 mg T-L/l in the Bass Island brine at Presque Isle, while D'Appolonia/IT measured <2 mg T-L/l for the same sample. The fact that only USGS measured significant levels of tannin-lignin at the Renkis well results in one of three conclusions with regard to this data. The USGS T-L measurements (38 and 73 mg/l) are either background levels or represent contamination in the samples at both sites. The third possibility would be that the USGS measurements are inaccurate or that the sampling and analytical problems created highly variable results among all of the investigators. It is interesting to note, however, that if the tannin-lignin levels mentioned above are indicative of background contamination, then the dilution of the pulping wastes with brine is 1766:1 (using the average of the USGS data). This ratio would represent such a large dilution that few analytical parameters would be useful in supporting this theory. There is not sufficient information available to further evaluate the methods or the results at this time.

The information resulting from the work of Cooper-Driver and Wilson (EPA, 7/4/84) is not presented in Table 5-7. The data are complex and do not lend themselves to this format. The reader is referred to the original report if needed. Their lignin analyses were performed by using a cupric oxide oxidation technique. The amounts and types of compounds derived from the oxidation are indicative of the lignin originally present in the sample. In their work, they demonstrated the lack of lignin solubility at the 1 ug/l concentration level in the water samples. Due to lignin's known insolubility, they analyzed both the water and the suspended sediments in the samples. In their conclusions, they noted a limited presence of lignin at the sites in concentrations typical of or lower than many geochemical samples. Since no elevated amounts of lignin were observed in the samples, one can conclude either: (1) no pulping wastes have reached the site, (2) if pulping wastes are present, there has been a large dilution with brine, or (3) if pulping wastes are present, then the lignin was removed by adsorption onto particulates en route to the sites.

Samples from the seep, Bass Island Formation, and Lockport Formation were analyzed for Busan (a microbicide) and its components (Krokenberger/IT, 1984). The report noted rapid degradation (completely degraded after 2 days) of the mixed active ingredients and formation of a reaction product. From their time studies, they concluded that the reaction product could not be used as a tracer for Busan in unextracted environmental samples. The report indicated that Busan was not detected in the environmental samples. The samples apparently were not extracted due to difficulties with the procedure. Further evaluation of the presence of Busan in the samples cannot be made at this time. No detection limits and very little quantitative information were available in the report.

Gas chromatographic (GC) "fingerprint" analyses were performed on some of the samples by Garnas (EPA, 2/18/84). In the summary, he noted pattern matches on sample extracts for the seep and the Bass Island Formation but not on the Lockport Formation, Renkis Gas well, or the bailer blanks. Reference pulp liquors (such as Neutracel I) and samples from the East High School well were not available to Dr. Garnas for analyses. Nottingham (EPA, 10/11/84) performed the same fingerprint analysis on a sample from the East High School well. The analyses resulted in a fingerprint that did not match those from the Presque Isle site. The intent of the work was to show a unique constituent in a contaminated brine common to the Presque Isle samples. The results did not prove a connection between the two sites. However, since the origin of the fingerprint is unknown, the results cannot be used to disprove the presence of the pulping liquor at the Presque Isle site.

## 6.0 HYDROGEOLOGY AND MODELING

### 6.1 Summary and Conclusions

This section reviews the mathematical approaches that have been used to describe the flow of injected pulping liquor wastes in the Bass Island Formation and the potential influences the Hammermill injection program may have had on the Presque Isle Beach No. 7 well (hereinafter called "the Beach No. 7 well").

Key discussions about aquifer hydraulics, subsurface movement of the injected pulping liquor waste, or contaminant transport are reviewed in this section.

The subsurface zone that received the injected wastes may include the Bass Island Formation and the Bois Blanc Formation. In this section, we do not distinguish between the two formations; thus the term "Bass Island Formation" refers to the entire subsurface zone that received injected wastes.

The terms "model" or "modeling" are used broadly in this section. For example, any mathematically based approach that describes waste fluid, formation fluid, or ground-water movement is referred to as a "model" in this section.

The following text will refer to pressure in the formation that could be expressed as force per unit area. A relationship exists between the expressions for formation pressure in pounds per square inch (psi) and an equivalent head of fluid. One atmosphere of absolute pressure is about 14.7 psi (pounds per square inch) and can support a 33.9-foot column of water at sea level (Daugherty and Franzini, 1977). This corresponds to a vertical pressure gradient of 0.434 psi/ft. If the fluid of interest is other than pure water, the relationship is modified to account for the difference in specific gravity. For example, formation water in the Bass Island Formation has a specific gravity of 1.2 (Walker-PADER, 8/15/83). The vertical pressure gradient of a column

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of Bass Island brine is 0.520 psi/ft. The pulping liquor has a specific gravity of 1.02 (Walker-PADER, 8/15/83) so its vertical pressure gradient is 0.442 psi/ft.

A numerical model called NEMESIS, which stands for Numerical Engineering Model Evaluating Subsurface Interstitial Systems, was employed by a professional engineer to simulate contaminant transport under various combinations of reservoir conditions, hydraulic parameters, mixing parameters, and injection pressures appropriate for the Presque Isle setting (Koederitz-EPA, 5/8/84). Some results of simulations using the NEMESIS model, performed on behalf of PADER, lead to the conclusion that injected pulping liquor from the Hammermill injection wells could reach the Beach No. 7 well, and flow through the annulus to the ground surface (Koederitz-EPA, 5/8/84). Another simulation using the model NEMESIS, when permeability equaled 65 millidarcies, identified that residual effects following the cessation of injection caused a pressure response to be present at the Beach No. 7 well through 1983 (Koederitz-EPA, 5/23/83).

The NEMESIS model is the only model used in studying the influence of flow at the Beach No. 7 well that incorporates influences of multi-phase flow, formation heterogeneity, aquifer anisotropy, compressible fluids, and well injection hydraulics (see also Section 6.6). Because of the appropriate sophistication and application of the NEMESIS model, we conclude it is the most reliable of all the modeling approaches used to study the flow of fluid at the Beach No. 7 well. However, the results of these simulations alone can not conclusively confirm that the injection of pulping liquor at the Hammermill site could have caused the flow of fluid. It would be possible to link Hammermill's waste injection program to the observed contamination at Presque Isle if the modeling results clearly indicated a causal relationship between pulping liquor injection and the Beach No. 7 well, and if the results of the geologic review, chemistry and geochemistry studies all supported the same conclusion.

It may be more important at this stage to be more concerned about whether the existence of pulping liquor waste in the Bass Island Formation could pose any future problems than whether their injection caused some problem in the past. At least two aspects of the presence of pulping liquor in the Bass Island should be considered: where are the injected wastes flowing, and what chemical changes do the wastes undergo in the formation. The chemical changes are not discussed here.

A common shortcoming of all the models used was the failure, or inability, to determine the potentiometric surface and flow direction of fluids in the Bass Island Formation (under natural flow conditions when there is no injection). The Bass Island Formation has a subsurface outcrop in southern Ontario and dips to the south-southeast (D'Appolonia/IT-HML, 3/83). This may influence the flow direction but does not indicate the flow direction. The injected pulping liquor will probably migrate from the area in which it was injected. The rate and extent of the migration cannot be estimated without acquiring some site-specific information about the formation's hydrostatic head.

Three or more observation wells would have to be installed in the Bass Island Formation to generate sufficient information on the hydrostatic surface of the Bass Island Formation. These wells could allow the measurement of the potentiometric head in the formation and the periodic collection of samples of formation fluid. Such information would enable a more accurate projection of whether future problems may occur, but it would not necessarily resolve the lack of clear chemical and geologic evidence of the existence or nonexistence of a link between the seepage of fluid at the Beach No. 7 well and the Hammermill waste injection program.

## 6.2 Initial Dow Feasibility Study Model

Dow Industrial Service performed the initial feasibility study to ascertain whether pulping liquor wastes could be injected into the Bass Island and Lockport formations. Their efforts included the installation

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of Hammermill No. 1 test well and subsequent downhole geophysical logging measurements (Dow-HML, 11/19/62). Dow calculated the volume of pore space available in the subsurface to receive injected pulping liquor from the Hammermill operation. Dow also generated a diagram of concentric circles depicting the supposed advancement of the front of the injected fluid over time. The calculations and diagram are discussed below.

### 6.2.1 Purpose of Model Application

Dow Industrial Service was hired by the Hammermill Paper Company to assess the feasibility of using deep well injection to dispose of pulping liquor wastes that are generated during processing at the Hammermill facility in Erie, Pennsylvania. It appears that their primary objective was to demonstrate that deep well injection of wastes, which was a new technology at the time of the feasibility study, was a viable option for waste disposal. They based their arguments upon the assumption of a uniform, interconnected porous volume in the subsurface formation that would receive the wastes (Dow-HML, 11/19/62).

### 6.2.2 Major Assumptions

When this early feasibility study was done, very little specific information on the subsurface geologic structure of the Bass Island Formation, or on the formation's hydraulic properties and chemical nature, was known. Dow Industrial Service identified the subsurface formations of interest as the Bass Island and Lockport dolomites. Their calculations implied that the formations have interconnected pore spaces and are isotropic, homogeneous, and infinite, so the injected fluids flow equally in all radial directions from the injection well. They also assumed that formation fluids would be completely displaced by the injected wastes and there would be no resistance to the injected fluid. Furthermore, their calculation of injection fronts at various times is based on the assumption that flow in the porous medium is not limited by formation permeability.

6.2.3 Selection of Parameters

Dow Industrial Service assumed different values of formation thickness and porosity to calculate the advance of the injection front and the subsurface porous space available to receive injected wastes (Dow-HML, 11/19/62).

Subsurface Volume Available

Dow Industrial Service calculated the pore space available within a 1-mile radius (r) of the injection well. They assigned a formation porosity value (n) of 0.20 and formation thickness (B) of 100 feet. Then the subsurface volume available to receive injected wastes is simply the product ($3.14 \bullet r^2 \bullet B \bullet n$), which is 1,750,000,000 cubic feet or 13,100,000,000 gallons. This calculated volume is very large, which caused Dow to conclude the subsurface formation was a "satisfactory disposal reservoir" for Hammermill's pulping liquor wastes (Dow-HML, 11/19/62). In fact, if the subsurface volume available for waste disposal was so great, continuous injection of wastes at 350 gallons/minute (gpm) would not exhaust the storage space for 7 years.

It appears that Dow Industrial Service made an error in the calculations, because they reported the values as 1,550,000,000 cubic feet and 11,600,000,000 gallons (Dow-HML, 11/19/62). However, this discrepancy causes no change in the conclusion drawn by Dow Industrial Service.

Dow selected an aquifer thickness of 100 feet and felt that the actual thickness of porous spaces could be even greater (Dow-HML, 11/19/62). However, they had reason to believe the effective formation thickness could be less than 100 feet. Their study of the Hammermill No. 1 test well revealed that formation water flowed from a thickness of only 45 feet of the Lockport Formation (Dow-HML, 11/19/62) and from a thickness of only 35 feet of the Bass Island Formation (Dow-HML, 11/19/62). Dow sealed the lower portion of the test well, that part open to the Lockport Formation, with cement (Dow-HML, 11/19/62), so only the

Bass Island Formation should have been considered in their estimate of formation thickness. The calculation of subsurface volume available within a 1-mile radius in a 35 foot thick formation, assuming the same porosity value of 0.2, decreases the calculation for available pore volume to 613,000,000 cubic feet, or 4,590,000,000 gallons, or about 3 times less than the volume calculated by using a 100 foot thick formation.

Calculation of the Injection Front

By assuming that the injected fluid moved outward radially from the injection well at the same rate at which it was injected, Dow Industrial Service was able to calculate the radii of the injection fronts at various times since the start of injection. Dow assumed that the constant injection rate (Q) would be 350 gpm, the formation thickness (B) was 50 feet, and the formation porosity (n) was 0.15 (Dow-HML, 11/19/62). In this application, their objective was to calculate the radii of the pore volumes that would be filled with injected wastes after 1, 5, 10, 20, 30, 40, and 50 years of continuous, constant injection. The equation for this calculation is

$$r = [(Q \bullet t)/(3.14 \bullet B \bullet n)]^{0.5}$$

where t is time. When appropriate unit conversions are applied, the radius calculated at 1 year is 0.194 mile; at 5 years, it is 0.433 mile; and finally, at 50 years, it is 1.37 miles (Dow-HML, 11/19/62).

6.2.4 Strengths and Weaknesses of Approach

The above calculations are based on simple, straight-forward geometric and continuity relationships. They are easy to visualize and to understand. As a first estimate of the maximum subsurface pore space available, the approach is reasonable.

However, no site-specific information was used in the calculations, and no attempt was made to modify the equations or input parameters to improve the applicability of the approach. If, for the sake of discussion, it is assumed that only one-half of the 35-foot porous zone in the Bass Island Formation was available for the effective distribution of injected wastes, and the effective porosity was one-half of the assumed 0.15 (because the injected fluid does not completely replace the formation fluid), then the injection front could advance a radial distance of 0.5 mile in the first year. At 5 years, the front would be at a radius of 1 mile, and at 50 years, it would be over 3 miles from the injection well.

The physical nature of the formation fluid in the Bass Island Formation, its specific gravity and ability to mix with the injected wastes, was not considered in the above calculations. For example, we now know the formation fluid is more dense than the injected pulping liquor (Walker-PADER, 8/15/83). This fact means it is less likely that the injected wastes would completely mix or replace the formation fluid, but they would instead flow or migrate toward the top of the porous zone. The existence of two separate phases of fluids having different densities would be even more pronounced at distances from the injection wells where flow is laminar (near the well, there are probably much turbulence and mixing). In addition, the formation's potentiometric surface and flow field were not considered in this approach.

### 6.2.5 Overall Reliability of Approach

The approach used by Dow Industrial Service can only be viewed as a rough, first estimate of the pore space available to accept injected wastes and of the rate of advance of the injection front. The assumptions of formation homogeneity and isotropy, of radial flow, and of fluid displacement are not realistic. The calculations do not use formation porosity and thickness values that are representative of the Bass Island Formation. The calculations are based upon cylindrical volumes that are probably not representative of the actual distribution of injected wastes in the Bass Island Formation.

## 6.3 Hagen-Poiseuille Law for Laminar Flow

PADER applied the Hagen-Poiseuille equation for laminar flow in a circular pipe to ascertain whether the flow observed at the Beach No. 7 well could possibly be due to the flow of injected wastes along a fracture from one of Hammermill's injection wells to the Presque Isle well (Hellier-PADER, 10/11/79; Walker-PADER, 8/15/83). The Hagen-Poiseuille is an equation from fluid mechanics that is used to calculate the head loss as a function of flow velocity in a pipe, or to calculate discharge given the head loss along a pipe of known radius and length (Daugherty and Franzini, 1977). The application of this equation to fracture flow is based upon the supposition that fluids in the formation will behave more like fluids flowing through pipes than through unconsolidated, porous media.

### 6.3.1 Purpose of Model Application

PADER sought to demonstrate that Hammermill's waste injection program could cause the flow of fluid from the Beach No. 7 well. They were also attempting to find an appropriate way to describe fluid movement in a consolidated formation believed to be fractured (Walker-PADER, 8/15/83).

### 6.3.2 Major Assumptions

Application of the Hagen-Poiseuille equation assumes that flow in a fracture is laminar; that is, the head loss due to friction varies directly with velocity. The Reynold's number must be less than 2,000 for laminar flow to exist (Daugherty and Franzini, 1977). Because the application is taken from circular pipe flow theory, it implies that the supposed fractures can be approximated by tubes or imaginary pipes.

### 6.3.3 Selection of Parameters

PADER assumed that the observed flow rate of fluid from the Presque Isle well 7, about 400 gallons/day, was due solely to the delivery of injected wastes transported through a fracture of unknown dimensions

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(Hellier-PADER, 10/11/79). PADER also assumed that the head loss along a hypothetical pipe (the fracture) was equal to the difference between the injection pressure and atmospheric pressure at the Beach No. 7 well (Hellier-PADER, 10/11/79). The Hagen-Poiseuille equation is given by

$$Q = (3.14 \bullet r^4 \bullet h_L \bullet P \bullet g)/(8 \bullet u \bullet L)$$

where $Q$ = discharge rate, 400 gallons/day
$r$ = effective radius of the fracture, unknown
$h_L$ = head loss along the pipe (fracture), 1200 psi
$P$ = density of the fluid, assumed to be 1 gram/$cm^3$
$g$ = acceleration due to gravity, 980 cm/$sec^2$
$u$ = dynamic viscosity of the fluid, assumed to be 1 centipoise
$L$ = length of the pipe (fracture), 4.2 miles

The values given here are those assigned by PADER (Hellier-PADER, 10/11/79). When these values are substituted into the equation and the appropriate unit conversions are employed, the calculated value of the radius is 0.25 cm. This solution means that a 4.2-mile long pipe of 0.5-cm diameter that delivers 400 gallons/day of water would experience a 520-foot (1,200 psi) head loss over its length. The pipe diameter is not limited to a 0.5-cm diameter. In fact, as the radius increases, the head loss decreases as the fourth power of the radius when all other factors remain constant.

PADER (Hellier-PADER, 10/11/79; Walker-PADER, 8/15/83) did not check their calculated diameter to see if the result met the assumption of laminar flow. The criterion for laminar flow is that the Reynold's number is less than 2,000. The Reynold's number is a dimensionless coefficient that represents the ratio of the inertial forces to viscous forces (Daugherty and Franzini, 1977). For applications in circular pipe flow, the Reynold's number, $R_e$, is given by

$$R_e = (D \bullet V \bullet P)/(u)$$

where $D$ = diameter, 0.5 cm
$V$ = discharge per cross-sectional area, 90 cm/sec
$P$ = fluid density, assumed to be 1 gram/$cm^3$
$u$ = fluid dynamic viscosity, assumed to be 1 centipoise

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A centipoise is defined as 0.01 gram/cm/sec. When these values are substituted into the equation for the Reynold's number, the resulting product is 4,500. This exceeds the criterion, which means that flow in the pipe (fracture) does not meet the requirements for laminar flow and the flow is turbulent.

The selection of the head loss parameter is somewhat misleading. There is an implied assumption that the pressure of the injected fluid at the injection well screen is equal to the surface pressure in the operating pump, or about 1,200 psi (D'Appolonia/IT-HML, 3/83, Table 1). The pressure in the Bass Island Formation at the Beach No. 7 well is apparently equal to or greater than 700 psi (HML, 7/27/79) if fluid is flowing to the surface there. Substituting a head loss of 500 psi into the Hagen-Poiseuille equation and keeping the other terms the same yield a calculated radius of 0.31 cm. Though this value is a reasonable value for the dimension of a fracture, the underlying assumption of a single fracture connecting an injection well to the Beach No. 7 Well is tenuous. Its shortcomings are discussed further below.

PADER selected dynamic viscosity and fluid density values equal to that of water rather than those of the pulping liquor or formation fluid.

### 6.3.4 Strengths and Weaknesses of Approach

The Hagen-Poiseuille equation could be used effectively to approximate the discharge, or its related velocity, of fluid flowing through a fracture that behaves hydraulically as a pipe. Such applications would imply that the frictional head losses along the fracture and the geometry of the fracture are known.

The input parameters used by PADER could be modified in many ways to reflect conditions more reasonable than the existence of a single fracture, such as well discharge due to multiple but similar fractures so that discharge in any one fracture is some fraction of 400 gpm. This type of assumption would help keep the resulting Reynold's number within the critical range (less than 2,000). It would also be reasonable to

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assume that the flow path is longer than 4.2 miles (branching fractures rather that one straight fracture) or that the frictional head loss along the flow path is less than the total difference in pressure heads observed at the two wells (additional head losses before the fluid reaches the flow path). These types of combinations of parameters make it evident that any parameter values could be substituted into the Hagen-Poiseuille equation to generate values of fracture radii, but the exercise would be meaningless, because there is no unique result that is correct.

### 6.3.5 Overall Reliability of Approach

The application of the Hagen-Poiseuille equation is an interesting attempt to describe fluid movement in a porous medium that is consolidated and nonuniform. However, its application neither proves nor disproves the existence of fracture flow in the Bass Island Formation. Furthermore, the analysis is based on nonsupportable assumptions such as a single (or few), direct fracture pathways between the injection well(s) and the Beach No. 7 well.

## 6.4 D'Appolonia's Calculations for Aquifer Pressure, Velocity Flow Field and Steady State Concentrations

An Interim Report of the Presque Isle State Park Gas Well Investigation (D'Appolonia/IT-HML, 3/83) contained results of calculations for ground-water flow during and following injection at the Hammermill injection wells and calculations for contaminant transport from the area of the injection wells. These calculations were part of D'Appolonia's assessment of the relationship between the Hammermill waste injection program and seepage observed at the Beach No. 7 well. D'Appolonia performed these calculations on behalf of Hammermill (D'Appolonia/IT-HML, 3/83).

### 6.4.1 Purpose of Model Application

D'Appolonia/IT-HML (3/83) sought to calculate the pressure head build-up and decline in the Beach No. 7 well due to Hammermill's well

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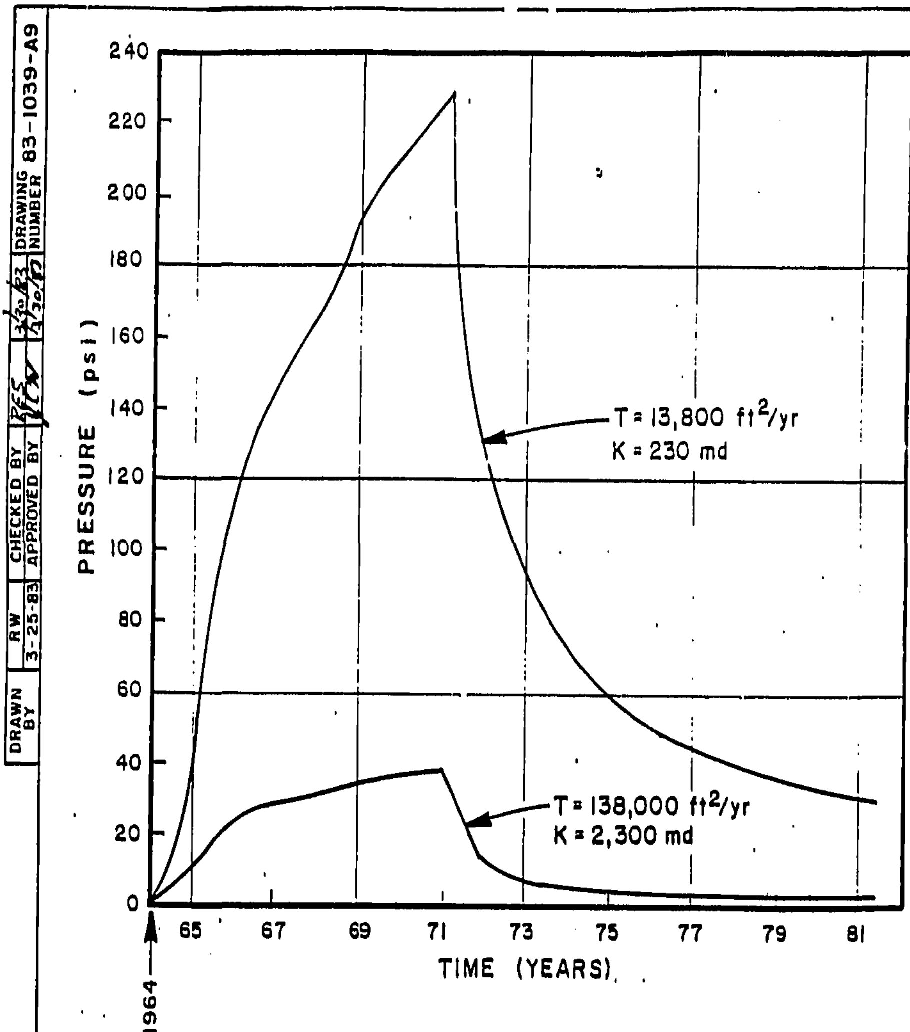
injection program and its cessation, and to calculate concentration isopleths caused by the injection of pulping liquor. The purpose of their efforts was to establish whether the injection could cause the well head pressures and contamination observed at the Beach No. 7 well. Their calculations involved three separate aspects of analysis: (a) calculating the change in formation pressure due to fluid injection and cessation, (b) the velocity flow field during injection, and (c) the distance to concentration isopleths. The calculations for each are summarized in the following three paragraphs.

Formation Pressure

D'Appolonia (HML, 3/83) used the Theis equation, for unsteady flow to a well in a confined aquifer, and the principle of superposition to calculate the pressure build-up at radial distances from an assumed, effective central location of the injection wells at Hammermill Industries. The principle of superposition applies to functions that have a linear relationship with each other and allows the final solution to a mathematical problem to be achieved as a sum of solutions that are valid for parts of the problem (e.g., Bear, 1979). D'Appolonia calculated the increase in pressure that could occur at the radial distance (about 4.2 miles) to the Beach No. 7 well during the injection period from 1964 to 1971 to ascertain whether pressures observed at the Beach No. 7 well could be due to injection of fluids at the Hammermill injection wells.

D'Appolonia used two estimates of aquifer permeability to encompass the range of values they considered appropriate to the Bass Island Formation (D'Appolonia/IT-HML, 3/83). They concluded that the maximum pressure caused by waste fluid injection in the Bass Island Formation would range from about 40 psi to about 230 psi at the Beach No. 7 well, as shown here in Figure 6-1 (D'Appolonia/IT-HML, 3/83). They also concluded that the pressure at the Presque Island well in 1983 (when the report was written) should range between 5 psi and 30 psi, as shown in Figure 6-1 (D'Appolonia/IT-HML, 3/83). The range in the calculated




NOTE:

T = TRANSMISSIVITY
K = PERMEABILITY IN MILLIDARCIES(md)
CURVES CALCULATED FOR:
STORAGE COEFFICIENT $1.0 \times 10^{-5}$
RESERVOIR THICKNESS 60 FEET

FIGURE 6-1
BUILDUP AND DECLINE OF PRESSURE (IN PSI)
IN THE PRESQUE ISLE BEACH NO. 7 WELL
FROM MAY 1964 TO 1981 DUE TO
HAMMERMILL WASTE INJECTION PROGRAM
Source: D'Appolonia/IT-HML, 3/83.

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pressure build-up and decline was accomplished by using the two estimates for aquifer permeability.

Velocity Flow Field

D'Appolonia used a two-dimensional, finite difference model called "GEOFLOW" to calculate the steady state velocity flow field in the Bass Island Formation around the Hammermill injection wells during the period of injection (D'Appolonia/IT-HML, 3/83). The results of their calculations are shown in Figure 6-2. D'Appolonia (3/83) used a time-weighted average injection rate to calculate values of pressure head at a radius equivalent to the approximate distance between the Hammermill injection wells and the Beach No. 7 well. The time-weighted average injection rate was given as 300 gpm (D'Appolonia/ IT-HML, 3/83), and the distance between the Beach No. 7 well and the Hammermill injection wells was given as 4.2-4.5 miles (D'Appolonia/IT-HML, 3/83).

Revision 4.1 of the GEOFLOW code (IT, 1986), which Versar reviewed, is a coupled flow model for ground-water flow and contaminant transport. Revision 4.1 of GEOFLOW could be used to calculate both the velocity flow field and the concentrations at all locations in the flow field. However, D'Appolonia (IT-HML, 3/83) used only the ground-water flow portion of GEOFLOW to calculate the velocity field. This may imply that an earlier version of GEOFLOW available in 1983 did not include the code for contaminant transport.

Concentration Isopleths

D'Appolonia's results from the ground-water flow portion of GEOFLOW, shown in Figure 6-2, were used to estimate a constant pore water velocity set equal to the average value within 1,400 feet and 25,500 feet of the injection wells (D'Appolonia/IT-HML, 3/83). The resulting estimated velocity was 40.8 feet/year, which was assumed to be uniform and constant (D'Appolonia/IT-HML, 3/83).

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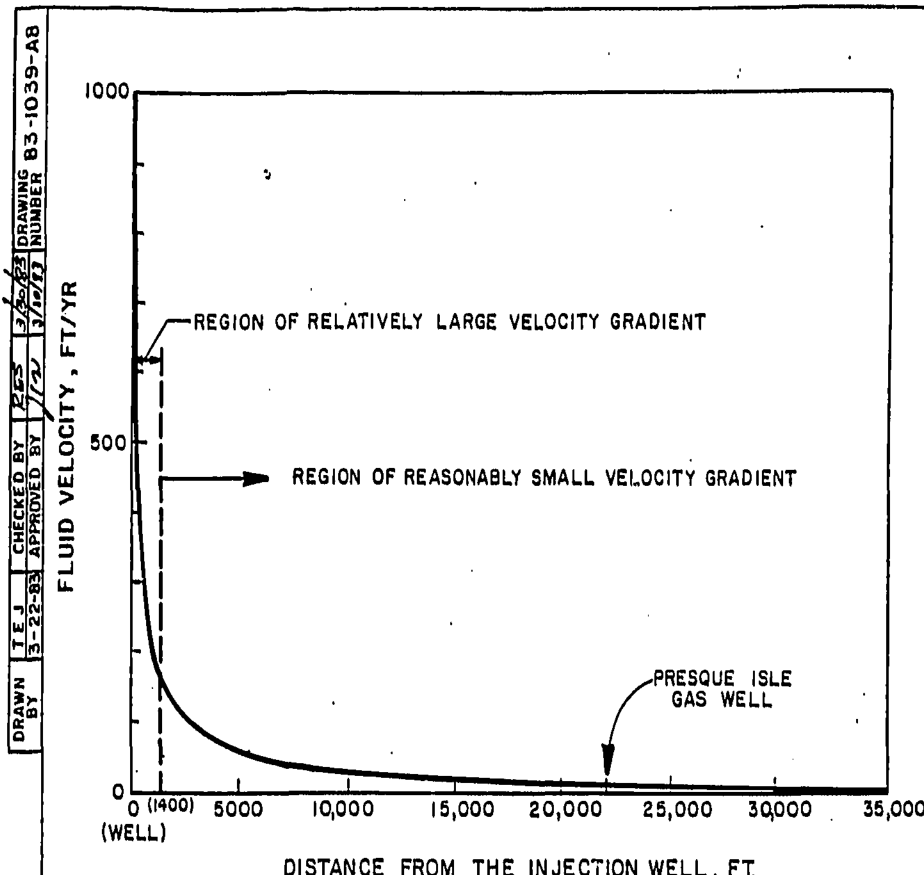


FIGURE 6-2
VELOCITY FLOW FIELD IN BASS ISLAND FORMATION DURING THE HAMMERMILL WASTE INJECTION PROGRAM

Source: D'Appolonia/IT-HML, 3/83.

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The assigned value of velocity was used to calculate concentrations within the Bass Island Formation by using a simplified version of an analytical solution developed by VanGenuchten and Alves (1982) for one-dimensional contaminant transport from a constant, continuous source in a homogeneous aquifer that has a steady state, uniform flow field. D'Appolonia calculated the distance at which the relative concentration isopleths would be equal to 0.01, 0.1, and 0.5.

One calculation was performed using a time interval of 7 years to represent the start of waste injection at Hammermill well 1 in 1964 and the cessation of all injection in 1971. A second calculation was performed using a time interval of 12 years to represent where the contaminant isopleths would be located if the assumed flow velocity during injection had continued to the time the report was written. They based this latter calculation on the conservative assumption that the pore water velocity in the formation remains constant following the cessation of injection (when, in fact, it will decline).

D'Appolonia described the calculation as a conservative estimate of contaminant transport, presumably because the analytical solution assumes the source is constant and continuous and because they calculated the concentration isopleths at time intervals of 7 and 12 years (corresponding to the injection period from 1964 to 1971, and a conservative estimate of assuming continued injection through 1983). D'Appolonia also assumes the source concentration extends throughout a 3,400-foot area from the source (D'Appolonia/IT-HML, 3/83).

### 6.4.2 Major Assumptions

D'Appolonia's approach for the 1983 report necessitated the assumptions that the aquifer (the Bass Island Formation) is isotropic and homogeneous and that the hydraulic conductivity and transmissivity are constant throughout the aquifer. The application of the Theis equation assumes radial flow around the injection wells and that there are no boundaries throughout the formation (an infinite aquifer). All of their

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applications assumed that the aquifer flow was described by a single fluid (no consideration for displacement of fluids having different densities). It was further assumed that the fluids of concern, the formation and injection fluids, are incompressible. The application of the Theis equation assumes that the injection rates are constant though the periods of injection are discontinuous.

The application of the GEOFLOW code to calculate the velocity flow field assumes that the aquifer had reached a steady state flow condition (though the velocity was nonuniform). The selection of one value to represent an effective uniform velocity present at the Beach No. 7 well required the assumption that one velocity could accurately describe contaminant transport. The calculation of concentration isopleths assumes one-dimensional, steady state, uniform ground-water flow in a homogeneous, isotropic aquifer. The analytical solution used to calculate concentrations requires that diffusion be negligible with respect to dispersion (a reasonable assumption) and that the contaminant not decay or not be adsorbed by the aquifer medium (a conservative assumption). The simplifications that D'Appolonia employed to remove the exponential term in the solution equation required that the value of time used be very large (which is true).

### 6.4.3 Selection of Parameters

D'Appolonia selected two values of permeability to represent a range of permeability from 230 to 2,300 millidarcies (one darcy is about $10^{-8}$ $cm^2$) in the Bass Island Formation (D'Appolonia/IT-HML, 3/83). DOW Industrial Service found the permeability in the formation at Hammermill injection well 1 to be 2,300 millidarcies based on borehole tests (Walker-PADER, 8/15/83). A formation permeability of 230 millidarcies is based on a 1974 EPA estimate of the average permeability value for the Bass Island Formation (D'Appolonia/IT-HML, 3/83). D'Appolonia regarded the higher value, 2,300 millidarcies, as a maximum value for permeability of the formation if fracturing had occurred (D'Appolonia/ IT-HML, 3/83). To calculate the aquifer hydraulic conductivity, they used a fluid specific gravity of 1.0. The calculated hydraulic conductivity is 0.63 feet/day (1.93 cm/day) to 6.3 feet/day (19.3 cm/day) by using the range of permeability from 230 to 2,300 millidarcies.

D'Appolonia set the aquifer storativity ($10^{-5}$) and formation thickness (60 feet) to values they considered to be lower bounds (D'Appolonia/IT-HML, 3/83). The calculated value for aquifer transmissivity is the product of aquifer thickness and hydraulic conductivity. D'Appolonia gave the transmissivity value as being 13,800 to 138,000 $ft^2$/year (D'Appolonia/IT-HML, 3/83). The specific gravity of Bass Island fluids ranges from 1.182 to 1.193 (D'Appolonia/IT-HML, 3/83), and the specific gravity of the injected pulping liquor is about 1.02 (Walker-PADER, 8/15/83). The dynamic viscosity values associated with either of these fluids is not given.

The hydraulic conductivity calculated by using a specific gravity of 1.02 or 1.2 will not differ significantly from the value calculated when assuming the specific gravity is 1.0. Calculations of hydraulic conductivity from permeability are far more sensitive to values of viscosity, and if those values are known for the formation water or the injected pulping liquor, they could generate significantly different values of hydraulic conductivity.

The value of transmissivity was calculated by using an assumed aquifer thickness of 60 feet. D'Appolonia reported that the total thickness of zones of high porosity in the Bass Island Formation (defined as lying within the zone below the Onondaga Formation and above the Salina Formation) is about 10 to 18 feet (D'Appolonia/IT-HML, 3/83). The effective thickness of the porous portions of the Bass Island Formation is about 20 feet (Walker-PADER, 8/15/83). If the aquifer thickness was assumed to be 20 feet, the resulting calculated transmissivity would be 4,600 to 46,000 $ft^2$/year. This more appropriate range for transmissivity is 3 times smaller than the range used by D'Appolonia, but its effect on the resulting calculations is not linear.

Application of the Theis equation and Principle of Superposition was employed by using the lower limit of the range, 4,600 ft $^2$/year, to calculate what the pressure head would be at a well 4.2 miles from the injection wells in 1971, after 7 years of injection at well 1, 3 years of injection at well 3, and 3 years of injection followed by 3 years of recovery at well 2. The resulting pressure head due to the injection is about 1,240 feet of head, which is equivalent to 540 psi for a fluid having a specific gravity of 1.0, or 640 psi for a fluid whose specific gravity is 1.2. The value 540 psi can be compared to 230 psi which is pressure calculated by using the transmissivity of 13,800 ft$^2$/year (D'Appolonia/IT-HML, 3/83). This comparison reveals that the calculated pressure increases by a factor of about 2.3 when the lower transmissivity value is used.

### 6.4.4 Strengths and Weaknesses of Approach

The Theis equation is used to calculate changes in head at radial distances from pumping or injection wells under conditions of unsteady flow in an aquifer (Bear, 1979). Its application assumes that flow from the injection wells advances radially from the injection point and that the formation exhibits no resistance to the injected fluid. This approach can give estimates of maximum possible head changes, but its use as a representation of actual values for the Bass Island Formation is invalid, because it is not a homogeneous, isotropic formation with constant thickness, permeability, and storativity.

The sensitivity of the Theis equation to reducing the transmissivity value was demonstrated above. Similar types of calculations could be made for the formation storativity, which was given an assumed value of $10^{-5}$. The storativity of a confined aquifer could vary by an order of magnitude. For the calculation using transmissivity of 4,600 ft$^2$/year given above, decreasing the storativity value by a factor of 10 while

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keeping the other parameters constant will increase the calculated pressure head by a factor of 5.

The application of the simplified analytical solution (VanGenuchten and Alves, 1982) for one-dimensional contaminant transport is an acceptable first attempt to bring concepts of advective and dispersive transport into the discussion of a possible causal relationship between the observed contamination at the Beach No. 7 well and the Hammermill injection wells. The equation assumes a steady state, uniform flow field, so its application necessitated an assumption of a constant pore water velocity. The selection of a value for pore water velocity from Figure 6-2 was arbitrary. It would be just as reasonable to select a value of 100 feet/year or 25 feet/year as the pore water velocity that could effectively represent transport of contaminants to the Beach No. 7 well.

This approach also necessitated assigning a value for the coefficient of dispersivity, assumed to be 1 foot (D'Appolonia/IT-HML, 3/83). However, there is evidence that field dispersivity could be a function of the scale of study (Gelhar et al., 1985). If the effective coefficient dispersivity for this site was one-hundredth the scale (4.2 miles), its value would be 220 feet. If this value was substituted into the final, simplified equation given by D'Appolonia, the distance at which the concentration is one-hundredth the source concentration is 1,100 feet. If the larger dispersivity value of 220 feet and a velocity of 100 ft/year are used, the distance to the isopleth of one-hundredth the source concentration becomes 2,000 feet. Employing these conservative but reasonable estimates of parameters still does not cause the isopleth to approach the area of concern located about 22,200 feet from the injection wells. Thus, if the velocity flow field calculated by GEOFLOW is an accurate evaluation of pore water velocity responsible for advective transport and if the approach is reliable, then it does not seem that detectable concentrations of the injected pulping liquor would reach the Beach No. 7 well.

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6.4.5 Overall Reliability of Approach

Using the Theis equation and Principle of Superposition, D'Appolonia generated calculated values of pressures that were treated as if they were the actual pressures within the formation at given increments of time (D'Appolonia/IT-HML, 3/83, p. 5-4) instead of the change in pressure head due to the injection. If the Bass Island Formation has some hydrostatic pressure, which is probable since it is a confined aquifer, the pressures calculated above and shown in Figure 6-1 should be added to the formation's hydrostatic pressure to yield the pressure in the Beach No. 7 well that could force fluid to the ground surface. However no values of the Bass Island hydrostatic pressure are known, so the total pressure at the Beach No. 7 well cannot be determined.

Calculations of pressure head changes using the Theis equation were found to be sensitive to changes in the formation transmissivity and storativity. The sensitivity of the resulting calculation to the natural variability of uncertain input parameters indicates that the changes in pressure head calculated by this approach cannot be relied upon to draw conclusions about the influence Hammermill's injection wells have on pressure head at the Beach No. 7 well.

Transport in the Bass Island Formation may not be best described by hydrodynamic dispersion because the flow is not through an unconsolidated, isotropic, homogeneous medium. Mixing may not occur throughout the entire permeable thickness of the formation, because the contaminant may be more like a separate, immiscible phase. No consideration has been given to the effect of two fluids of different densities. In that case, the transport would not be described by the VanGenuchten and Alves (1982) analytical solution that was used.

6.5 Kleeman's Pressure Decline Calculations

EPA Region III employed another type of formation pressure calculation to estimate the influence that the Hammermill injection wells may have had on the Beach No. 7 well. Two values were calculated. One is based on the influence of Hammermill well 1 alone, and the second one is based on the concurrent operation of all three Hammermill injection wells.

6.5.1 Purpose of Model Application

The pressure decline calculation was performed to determine if the injection rate was sufficient to cause a flow of fluid from the Bass Island Formation at the Beach No. 7 well located 4.2 miles from the injection wells (Kleeman-EPA, 4/30/82). The approach and calculation were presented by Charles Kleeman as an incidental analysis prompted by the FIT Report review.

The source document (EPA-600/2-79-170) for this approach describes the equation used by Kleeman as a "pressure build-up" equation. Kleeman employs the equation as a pressure build-up equation, and it is not clear why Kleeman refers to the application of the equation as a "pressure decline" calculation (Kleeman-EPA, 4/30/82).

6.5.2 *Major Assumptions*

The governing theory for the equation used by Kleeman requires that fluids be injected into a confined, infinite, homogeneous, isotropic aquifer and flow radially from the injection well in a horizontal direction only. The theory assumes that the flow relationships can be described by a single fluid and that the fluid has a small, constant compressibility (EPA-600/2-79-170). Furthermore, it is assumed that the injected fluid is taken into storage instantaneously and the pressure effects are transmitted instantaneously throughout the formation (EPA-600/2-79-170).

6.5.3 Selection of Parameters

The pressure build-up at the Beach No. 7 well was calculated to be more than 200 psi after 6.5 years of waste injection from Hammermill well 1 operating alone (Kleeman-EPA, 4/30/82). The combined effect of the three Hammermill wells injecting concurrently but for different periods caused the pressure at the Beach No. 7 well to increase to 450 psi (Kleeman-EPA, 4/30/82). The parameter values that Kleeman used to calculate these pressures are given below.

Kleeman selected values for the formation thickness (75 feet), porosity (0.15), and permeability (230 millidarcies), that were later used in other applications (e.g. D'Appolonia/IT-HML, 3/83). Kleeman also used a value of dynamic viscosity for the fluid equal to 1.0 centipoise, which is the viscosity of water at 20 degrees Celsius and 1 atmosphere of pressure. However, Kleeman's rational for using this viscosity value included considering the formation temperature to be 73 degrees Fahrenheit and the formation water salinity to be 60,000 ppm (Kleeman-EPA, 4/30/82).

Kleeman assumed an injection rate of 350 gallons/minute in each Hammermill injection well and concurrent injection periods of 6.5 years for injection well 1, 3.2 years for injection well 2, and 2.8 years for injection well No. 3 (Kleeman-EPA, 4/30/82). This approach includes a factor for the compressibility of the formation water. Kleeman selected a compressibility factor of $3.2 \cdot 10^{-6}$ $psi^{-1}$ (Kleeman-EPA, 4/30/82).

The initial formation pressure, prior to the start of injection, was assigned the value of 725 psi based on the reported depth of injection well ID No. PA-2 being 1,611 feet and by assuming a pressure gradient of 0.45 psi/ft (Kleeman-EPA, 4/30/82). The pressure gradient of 0.45 psi/ft and formation pressure of 725 psi implies Kleeman was considering that the entire 1,611 feet was filled with pulping liquor which has a specific gravity of 1.2. However, the initial pressure value is supposed to represent the initial pressure in the formation prior to the start of injection, not the pressure in the injection well at the start of or during the injection (EPA-600/2-79-170). Kleeman may have assigned an inappropriate value for initial formation pressure because the value of 725 psi is assumed to be the hydrostatic pressure throughout the formation prior to injection.

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6.5.4 Strengths and Weaknesses

The equation to calculate the pressure build-up employs some parameters of well injection hydraulics, such as the system compressibility, formation volume factor, and skin factor (Kleeman-EPA, 4/30/82; EPA-600/2-79-170). The inclusion of these factors makes the calculation more specific and appropriate for the calculation of formation pressures during injection than the Theis equation used by Hammermill's consultants (D'Appolonia/IT-HML, 3/83).

The pressure build-up equation may be amenable to the Principle of Superposition, which would allow one to modify the equation to calculate formation recovery following periods of injection, or to calculate the influence of nonconcurrent, multiple well injection periods. However, the parts of the source document that Versar reviewed did not contain a discussion on such an application, and Kleeman employed the equation as if all three Hammermill wells were injecting pulping liquor concurrently during the final 2.8 years of a 6.5-year injection period. Though this assumption will generate a conservative (maximum) estimate of the pressure head increase at the Beach No. 7 well, the assumption is not technically accurate.

6.5.5 Overall Reliability of Approach

The approach introduced by Kleeman takes into consideration the effects related to aquifer compressibility and injection well hydraulics. However, the approach is limited by the same assumptions of single phase (single fluid), radial flow in an ideal aquifer that were also employed in the pressure calculations performed by D'Appolonia (see Section 6.4 above). The pressure build-up equation introduces some new parameters, such as compressibility, formation volume factor, and skin factor, for which site-specific values are not known and must be assumed.

A significant shortcoming of this application of the pressure build-up equation is that the calculation is based on concurrent injection periods, which does not account for the fact that Hammermill

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well 2 was not operating during most of the injection period for Hammermill well 3. Another failing of this approach, and of the others, is that no consideration is given to the hydrostatic pressures and flow direction in the Bass Island Formation prior to the initiation of Hammermill's waste injection program.

### 6.6 Koederitz's Applications of NEMESIS

All previous calculations or models are limited by the restrictive nature of the governing assumptions that require treating the approximation of pulping liquor and formation brine as one fluid (single phase), and flow in an ideal aquifer. The numerical model called "NEMESIS" (Numerical Engineering Model Evaluating Subsurface Interstitial Systems) is sufficiently sophisticated and flexible to minimize the numbers of restrictive assumptions that govern its applicability to the complex flow system at the study site.

#### 6.6.1 Purpose of Model Application

Numerical simulations of fluid flow in the Bass Island Formation were performed by Dr. L.F. Koederitz to establish whether waste fluids injected at the Hammermill wells could reach the Beach No. 7 well and then flow to the ground surface within the time frame of concern. Koederitz is a registered professional engineer in the field of reservoir engineering (Koederitz-EPA, 4/21/83). Koederitz performed model simulations for EPA Region III. The model used is a fluid flow simulator that can be used to evaluate pressure heads for multiphase flow in a heterogeneous, anisotropic formation.

#### 6.6.2 Major Assumptions

The NEMESIS model is a finite difference solution to coupled equations of multiphase flow through a porous medium. The model code uses an implicit formulation to solve for pressure through the grid network and an explicit formulation to solve for saturation.

### 6.6.3 Selection of Parameters

Koederitz performed multiple runs with NEMESIS and selectively varied parameters to observe what effect each had on the simulation results. Koederitz sought to maintain reasonable values of injection pressures (Koederitz-EPA, 5/11/84) and to use reasonable values of formation and hydraulic parameters. Many simulations using the NEMESIS model were performed using various combinations of aquifer thickness (permeable formation thickness) of 14 to 100 feet, formation porosity of 0.102 to 0.192, formation permeability of 23 to 230 millidarcies, skin factor of -8 to 0, and skin radius of 100 to 6,000 feet (Koederitz-EPA, 5/23/83). Koederitz also performed simulations in which permeability reduction factors from 0.001 to 0.1 were included to show the effect of perimeter plugging (Koederitz-EPA, 5/11/84).

### 6.6.4 Strengths and Weaknesses of Approach

The NEMESIS model is the most comprehensive model that has been used in the study of the Beach No. 7 well contamination problem. The model can handle many pertinent factors (e.g., two-phase flow, compressible fluids, well injection hydraulics, formation heterogeneity) that the previous approaches had been unable to address (Koederitz-EPA, 5/8/84). The many model runs that Koederitz performed illustrate the ability of NEMESIS to assess the influence of the input parameters and assumptions employed to describe the hydraulics of the flow system.

The NEMESIS model can handle immiscible or soluble phases by varying the value of the mixing parameter from zero (no mixing) to one (complete mixing). A mixing parameter of 0.5 was used in the simulations by Koederitz (5/8/84). When the model results indicate that the injected fluid reaches the Beach No. 7 well, it arrives as a partially mixed, partially separate phase. This approach is more realistic than assuming that the two fluids mix throughly. Therefore, this model's results, in Versar's opinion, are more appropriate than those of a transport model that assumes advection and dispersion of the pulping liquor mixed (or in solution) with the brine.

Two weaknesses of the NEMESIS model are its requirement for numerous site-specific parameters that are not known with certainty, and the sensitivity of the conclusions drawn when parameters are altered. Both of these aspects of the model are discussed in greater detail in the next section.

6.6.5 *Overall Reliability of Approach*

Of all the approaches reviewed, the application of the NEMESIS model is the most reliable approach to simulating the response of the Bass Island Formation to the initiation and cessation of Hammermill's waste injection program. The model appears to be generating realistic results that accurately depict the nature of flow within the formation.

The input data to the model are numerous, and site-specific data are not always known. The inability to know which values are the most appropriate for simulations is a shortcoming of all the calculations and modeling approaches discussed. In some cases, the choice of a parameter value more appropriate than another is clearly evident. For example, when the assumed formation thickness is increased from 20 feet to 75 feet, the simulation results indicate that the injected pulping liquor would not reach the Beach No. 7 well and injection at the Hammermill wells would not create sufficient pressure to cause flow of fluid from the Beach No. 7 well (Koederitz-EPA, 5/11/84). In this case, it is evident from drillers' logs and downhole tests that the permeable thickness of the Bass Island Formation is closer to 20 feet than to 75 feet (Walker-PADER, 8/15/83; D'Appolonia/IT-HML, 7/19/79). However, the actual values of key parameters are not known and their values may still be debated by parties to this controversy. The fact that entirely different conclusions can be drawn when two different but reasonable values of a parameter are used raises questions of whether the results from NEMESIS simulations can be conclusive in isolation.

## 7.0 CONCLUSION

### 7.1 Discussion

Four distinct possibilities can explain the seepage of hydrogen sulfide-bearing fluids at the Beach No. 7 well on Presque Isle: (1) Hammermill's spent pulping liquor or its constituents were forced to the surface under injection pressure, (2) Hammermill's spent pulping liquor or its constituents were forced to the surface under natural artesian pressure after migrating to the area, (3) a naturally occurring Bass Island brine was forced to the surface under Hammermill's injection pressure, or (4) the seepage was wholly a natural phenomena.

The first two possibilities cannot be conclusively supported by the available chemical evidence. Sample contamination, analytical problems, geochemical complexity, appropriate background comparison criteria, and the great amounts of time and distances involved make the chemical issue problematic. Even additional monitoring wells and further sampling would probably not resolve many of these issues. Chemical evidence indicates that even if the pulping liquor were present in any of the previous analyses, it would have been diluted greatly, beyond the level of statistical observation.

The second two scenarios are conceptually more simple, but the answers are no more clear. D'Appolonia (HML, 3/83) has presented evidence that the Bass Island Formation could conceivably flow under its own artesian pressure, but this hypothesis is largely unprovable for the Erie area, because the Hammermill injection program has altered the normal hydrogeologic regime. Other wells in the Erie area could be observed in order to garner information on the potentiometric surface of the Bass Island Formation. However, this would be an expensive undertaking. A minimum of three points, but realistically many more, would be required to make any conclusions about the hydrostatic level.

In D'Appolonia's (HML, 3/83) most sophisticated reservoir modeling and the modeling of all other investigators on both sides of the argument,

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it was noted that the Hammermill injection program could have substantially raised the formation pressure at the Beach No. 7 well. D'Appolonia's (HML, 3/83) presents a natural artesian flow model to explain fluid flows at the Beach No. 7 well. Considering the 800-1000 foot fill-ups of Bass Island Formation fluids (Dow-HML, 11/19/62), and that D'Appolonia (HML, 3/83) includes both the artesian flow argument and the pressure drive arguments in the same document, the most provable conclusion is that, at a minimum, the Hammermill injection program forced a naturally occurring fluid that was near the surface from the Beach No. 7 well. On two occasions, Hammermill and their consultants readily admitted that this was a direct implication of their previous studies (Brosig, and Wright-HML personal communication, 12/8/86, 12/10/86 respectively).

In order to fully address the ramifications of any potential actions that the EPA may wish to pursue in this matter, Versar will assume that CERCLA does apply to this site under SARA Section 104(a)(4) in developing criteria for the record of decision (ROD) and to the potential delisting of this site. Since the site was listed based on a reasonable cause and effect relationship, it is fitting that the same standard be applied in formulating the ROD and delisting petition.

### 7.2 Record of Decision: Remedial Alternative Selection

Long term source control measures identified in the Draft Remedial Action Master Plan (RAMP) (SRW-EPA, 11/83) have largely been accomplished as follows:

1. The only known source of seepage, the Beach No. 7 well, has been capped.
2. Ground water and soils surrounding the Beach No. 7 well do not pose a threat to the public (Weston-PADER, 7/1/80a and 7/1/80b), and fresh sand was brought in to minimize any possibility of exposure; there are no drinking water wells in use on the peninsula.

3. Other drinking water wells that may have been at risk have been sampled and have not been determined to be contaminated with pulping liquor wastes (Senovich-NUS/EPA, 5/2/82).

4. Therefore, no further migration pathways have been recognized.

The Draft RAMP (SRW-EPA, 11/83) also discussed the drilling of a deep monitoring well to depressurize the Bass Island Formation, but it was recognized that the "no action" or "minimum action" alternative might be selected based on a cost-effective analysis. To drill such a well would cost $150,000, and depressurizing the formation would require some installation to treat the formation fluids that flow back. Such an installation would have to be immense in order to simply treat the 1.1 billion gallons of injected pulping liquors. It would have to operate for many years, especially considering that the pulping liquor may have been diluted 10 to 200 times by the normal formation fluids. Additionally, the natural formation fluids in the underlying Lockport Formation are just as hazardous and present few problems to experienced oil and gas well drillers. Thus far, the only receptors that have been identified as at risk are the ones near the oil and gas drilling rigs that are actively drilling through the Bass Island Formation.

EPA (Shoener-EPA, 10/85), the potentially responsible party (PRP) (Andrews- HML, 12/20/85), and the state (Gorman-PADER, 9/5/86) agree that a deep well would be unnecessary and pose an environmental risk.

In the Draft RAMP (SRW-EPA, 11/83) two initial remedial responses were also recognized. They are (1) notifying local drillers of hazardous fluids in the Bass Island Formation, and (2) developing contingency plans to seal uncontrolled discharges. The RI/FS (Shoener-EPA, 10/85) lists only the first response as a recommendation, probably because most drilling rigs must have blowout preventers and drilling mud must be made available to seal formations, and the second recommendation of the Draft RAMP (SRW-EPA, 11/83) is unnecessary.

Versar sees two clear actions that EPA may wish two adopt in its ROD. They are (1) "minimum action" consisting of notifing local drillers and providing the local office of the PADER Bureau of Oil and Gas Management with an appropriate hydrogen sulfide meter for their exclusive use, and (2) the above "minimum action," with cost recovery sought from Hammermill Paper Company for the well-plugging and testing project, and other investigations.

7.3 Delisting Criteria

The Draft Guidance on Deletion of Sites from the National Priorities List (OSWER Directive 9320.2-3) states that the agency plans to delete from the NPL, sites that have been classified as completions and where all required response actions and performance monitoring has commenced.

In order for a site to be classified as a candidate for deletion there must first be a technical evaluation to determine if it satisfies the criteria for deletion. This report would serve as this technical evaluation. The National Contingency Plan (NCP) allows for site deletion when based on the Remedial Investigation. EPA (in consultation with the state) has determined that the release poses no significant threat to public health and that remedial measures are not appropriate. The Shoener (EPA, 10/85) and Gorman (PADER, 9/5/86) correspondence are sufficient to meet this criteria. Deletion of a site from the NPL does not preclude eligibility for subsequent government-financed or PRP actions if future conditions warrant such actions, and enforcement action may be taken if necessary.

If the "no action" alternative is selected, data must confirm that the site poses no significant threat to public health or the environment. Versar feels that this criteria is adequately met given the abundant drilling that took place during the late 1970s, the normal hazards inherent in drilling through the Bass Island and Lockport formations (Table 3-3), the high salinities normally encountered in Erie County ground water (Figure 3-14), the steps taken routinely by both drillers and the Erie County Bureau of Oil and Gas, and the assessment of hazard by Weston (PADER, 7/1/80a and 7/1/80b; NUS-EPA, 5/2/83; and Shoener-EPA, 10/85).

Versar therefore recommends that EPA Region III do the following:

1. Notify local Erie County drilling companies (Table 7-1) of the presence of hydrogen sulfide-bearing lines in both the Bass Island and Lockport Formations and the need for safety precautions.

2. Purchase sophisticated hydrogen sulfide testing equipment for use by the Erie County Oil and Gas Inspector to protect the citizens of Erie County and gather reliable information on whether hydrogen sulfide gases are escaping from the Bass Island Formation.

3. After these monitoring steps are in place, pursue delisting the site from the NPL.

TABLE 7-1

LOCAL ERIE COUNTY OIL AND GAS DRILLING COMPANIES

JAB Enterprises, Agent
1821 Nagle Road
Erie, PA 16510

Benedictine Sisters of Erie, Inc.
6101 East Lake Road
Harbor Creek, PA 16421

Charles L. Valone
185 Sunset Beach Road
Northeast, PA 16428

Algis Norvasia
12408 Kerr Road
Northeast, PA 16428

Vinyard Oil and Gas Company
20 Blaine Street
Northeast, PA 16428

Northeast Industrial Fuel Company
Smedley Street
Northeast, PA 16428

Lakeport Realty
1426 West 10th Street
Erie, PA

S.W. Jack
P.O. Box 697
Indiana, PA 15701

Fairman Drilling Company
Box 288
Dubois, PA 15801

Delta Drilling
R.D. No. 4, Box 132A
Indiana, PA 15701

International Petroleum Service Company
Box 547
Sheffield, PA 16347

Benchmark Oil, Inc.
212 North Third Street
Olean, NY 14760

Union Drilling, Inc.
P.O. Drawer 40
Buchhannon, WV 26201

Underwater Gas Developers
Box 428
Port Colburne, Ontario Canada

J & L Well Service
Newell Road
Dunkirk, NY 14048

Envirogas, Inc.
69 Delaware Avenue, Suite 900
Buffalo, NY 14202

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